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DEUTERIUM EXCHANGE AT TERMINAL BORON-HYDROGEN BONDS CATALYZED B--ETC(U)

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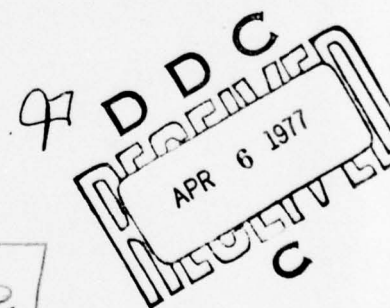
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Deuterium Exchange at Terminal Boron-Hydrogen Bonds Catalyzed
By Certain Transition Metal Complexes. A Qualitative Study of
Selectivity and Mechanism^{1,2}

by

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Abstract

A wide variety of substrates, including carboranes, metallocarboranes, and boron hydrides, were found to undergo catalytic isotopic exchange of terminal hydrogen with deuterium gas in the presence of various transition metal complexes. With $(PPh_3)_3RuHCl$ as catalyst, exchange was found to proceed with stereoselectivity indicative of nucleophilic attack at boron; *e.g.*, the order of rates for deuterium incorporation at chemically nonequivalent sites in $1,2-C_2B_{10}H_{12}$ was $B(3,6) > B(4,5,7,11) > B(8,10) > B(9,12)$. Other catalysts, most notably the series of hydridometallocarboranes, $(PPh_3)_2HMC_2B_9H_{11}$ ($M = Rh, Ir$), showed little or no stereoselectivity during deuterium exchange. Intermediate stereoselectivity was found with $(PPh_3)_2(CO)IrCl$ and $(PPh_3)_2IrCl$ species as catalysts, while exchange catalyzed by $(AsPh_3)_2IrCl$ exhibited the stereoselectivity found with $(PPh_3)_3RuHCl$. A mechanism is postulated which rationalizes the varied results and which involves oxidative addition of boron-hydrogen bonds to catalytic species.

Introduction

The first example of oxidative addition of a boron-hydrogen bond with a transition metal complex has been recently reported.⁴ This intramolecular reaction is best described as an ortho metallation of an L_3IrCl complex (L is the

Figure 1

carboranylphosphine $1-P(CH_3)_2-1,2-C_2B_{10}H_{11}$ (I)) and is analogous to well-known ortho metallations in arylphosphine complexes.⁵ This similarity led us to inquire if other reactions involving activation of aromatic C-H bonds, particularly the ortho deuteration reactions discovered by Parshall, Knoth and Schunn,⁶ might also take place in boron hydride chemistry.

The catalytic effectiveness of $(PPh_3)_3RuHCl$ for the deuteration of I was first studied. Wilkinson and coworkers reported that this transition metal complex can exchange all ortho hydrogen atoms for deuterium in the presence of D_2 ,⁷ and Parshall, et al. found it to be an effective catalyst for the specific ortho deuteration of excess PPh_3 .⁶ The results of these experiments and the extensive study of catalysis to which it led are described herein.

Although deuterium exchange on organic substrates often lends itself to quantitative study by either 1H nmr or mass spectroscopy, deuterium exchange in boron hydrides is much more difficult to quantify. The inherently broad line widths of the proton resonances in boron hydrides arising from complex spin-spin coupling interactions make 1H nmr valueless for the study of hydrogen-deuterium exchange. In addition, the complex isotope patterns and unreliable fragmentation schemes exhibited by boron hydrides in mass spectroscopy makes this technique generally unsuitable for exchange studies also. However, deuterium exchange is conveniently detected by both ir and ^{11}B nmr spectroscopy. The latter is a particularly useful probe as it readily distinguishes the sites at which exchange occurs. Most resonances are doublets due to spin-spin coupling of the

boron atom with its terminal hydrogen atom. The coupling of terminal deuterium to boron is essentially negligible in comparison to the broadness of the boron resonance, and the chemical shift upon substitution of deuterium for hydrogen is only barely detectable (ca. 0.05 ppm upfield). Thus, the exchange of hydrogen for deuterium at those sites represented by a given resonance may be followed by observing the smooth replacement of the doublet by a singlet with increasing incorporation of deuterium at those sites.

The present study was essentially exploratory in nature and although quantitative measurements of exchange were not obtained, qualitative estimates of the extent of exchange were made from examination of the ir, ^{11}B nmr, and mass spectra. The mechanistic deductions discussed herein are based on these observations and especially on analysis of the ^{11}B nmr spectra of deuterated species. The conclusions presented are well supported by the available data and by analogy to the proposed mechanism for catalytic exchange of aromatic C-H with D_2 .⁸

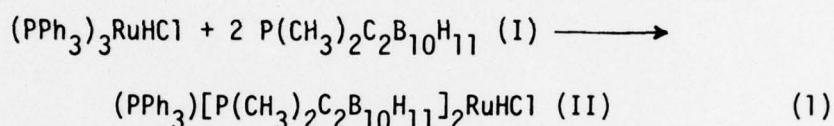
Results

Preparation and Characterization of $(\text{PPh}_3)[1\text{-P}(\text{CH}_3)_2\text{-1,2-C}_2\text{B}_{10}\text{H}_{11}]_2\text{RuHCl}$ (II).

Treatment of a purple suspension of $(\text{PPh}_3)_3\text{RuHCl}$ in toluene with excess $1\text{-P}(\text{CH}_3)_2\text{-1,2-C}_2\text{B}_{10}\text{H}_{11}$ (I) caused no immediate reaction. Upon warming to 80° , however, a red-orange solution formed. From the solution, a yellow-orange powder could be isolated whose elemental analysis agreed with that expected for $(\text{PPh}_3)[\text{P}(\text{CH}_3)_2\text{C}_2\text{B}_{10}\text{H}_{11}]_2\text{RuHCl}$ (II). In agreement with the analysis, the ^1H nmr spectrum (CD_2Cl_2) showed resonances in the τ 1.8-3.0 region (area 15), assigned to coordinated PPh_3 ; a broad singlet at τ 4.47 (area 2), assigned to carboranyl C-H; and two area 6 triplets (1:2:1) at τ 8.35 [J_{PH} (apparent) = 2.5 Hz] and τ 9.24 [J_{PH} (apparent) = 2.5 Hz] assigned to the methyl groups. The hydride was not located in the proton nmr, presumably because of the low solubility of the complex and the high multiplicity expected of the hydride resonance; however,

the ir spectrum clearly showed ν_{RuH} at 2020 cm^{-1} (compare to 2020 cm^{-1} for $(\text{PPh}_3)_3\text{RuHCl}$).⁹

These spectral data are consistent with II being a complex formed by simple ligand exchange of two equivalents of I for two of the three triphenylphosphines in the trigonal plane of trigonal bipyramidal $(\text{PPh}_3)_3\text{RuHCl}$ (eq. 1). For a molecule of this structure the carborane C-H resonances would be equivalent and the two methyl groups on each ligand would be chemically nonequivalent



to each other. However, each methyl group on a given ligand would be chemically equivalent to one of the methyls on the other carboranylphosphine, giving rise to two pairs of equivalent methyl groups. The ^1H nmr resonances for these groups appear as triplets due to virtual coupling. Virtual triplets are observed for methyl resonances in transition metal complexes with two equivalent methylphosphine ligands when $|J_{\text{PP}}| \gg ||J_{\text{PCH}_3} - J_{\text{P}'\text{CH}_3}||$.¹⁰ The correlation of multiplicities of methyl resonances with the stereochemistry of octahedral complexes of methylphosphines has been widely studied,¹¹ but to our knowledge no reports have appeared concerning trigonal bipyramidal complexes. Thus, the observed methyl triplets in the nmr spectrum of II could be due to such virtual coupling effects, but the presence of a third phosphorus ligand and of the unobserved hydride resonance do not permit an unequivocal interpretation of the spin system from these data.

Exchange of Deuterium Gas with 1- $\text{P}(\text{CH}_3)_2$ -1,2- $\text{C}_2\text{B}_{10}\text{H}_{11}$ (I) Catalyzed by II.

Deuterium gas was bubbled through a toluene solution of II containing excess I for 3 days at 100° . The phosphine then isolated from the solution was found to have been partially deuterated at boron by the presence of both ν_{BH} (2600 cm^{-1}) and ν_{BD} (1950 cm^{-1}) bands in its ir spectrum (melt on NaCl). The

same spectrum lacked any bands which could be assigned to ν_{CD} , implying no deuteration had occurred at C-H bonds. The relative absorbances of the ν_{BH} and ν_{BD} bands indicated ca. 40% deuteration or an average of four deuterium atoms per molecule. The low energy mass spectrum of the product confirmed the estimated average of four deuterium atoms per molecule, but revealed the presence of species with up to six deuterium atoms per molecule.

A mechanism incorporating deuterium into the ligand via ortho metallated intermediates, analogous to the mechanism proposed for ortho deuteration of triphenylphosphine by $(PPh_3)_3RuHCl$,⁶ could introduce a maximum of four deuterium atoms into the carborane cage of the phosphine, at positions 3,4,5, and 6 (cf. Figure 1). The presence of species containing more than four deuterium atoms per molecule ruled out intramolecular exchange of this type as the sole mechanism for deuterium incorporation.

Exploratory Deuterium Exchange Reactions.

To determine if noncoordinating carboranes would undergo isotopic exchange with deuterium gas as had been observed for the carboranylphosphine I, 1,2- $C_2B_{10}H_{12}$ and a catalytic amount of $(PPh_3)_3RuHCl$ were treated with excess deuterium gas at 100° in toluene solution for 3 days (system 1, Table I). The ir spectrum of the carborane product showed extensive deuteration at boron, but none at carbon. The relative absorbances of ν_{BH} and ν_{BD} indicated an average of six deuterium atoms per molecule.

Subsequently, a wide variety of noncoordinating substrates possessing terminal B-H bonds were found to undergo similar isotopic exchange in the presence of a number of group VIII transition metal catalysts. The conditions employed and the results obtained for a selected number of exploratory catalytic deuteration reactions are given in Tables I-III. Details pertinent to individual substrates and catalysts are discussed below.

Exchange with Carborane Substrates Catalyzed by $(PPh_3)_3RuHCl$.

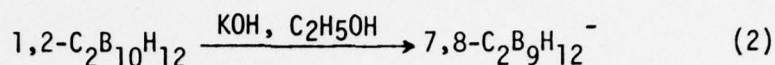
Table I gives the gross extent of exchange for the reactions catalyzed by $(PPh_3)_3RuHCl$. The catalyst could be recovered (usually in 40-60% yields) from the exchange reactions with carborane substrates and was found to be unchanged except for self-deuteration, rapidly forming the perorthodeuterated complex $[(2,6-D_2C_6H_3)_3P]_3RuDCl$.⁶ The exchange reactions catalyzed by this complex were found to exhibit stereoselectivity at nonequivalent sites in the substrates and no deuterium was introduced at carborane C-H by this catalyst (no ν_{CD} in ir spectra of deuterated products).

$1,2-C_2B_{10}H_{12}$. The structure of $1,2-C_2B_{10}H_{12}$ is shown in Figure 2. Symmetry requires the presence of four chemically nonequivalent sets of chemically equivalent boron atoms. The 80.53 MHz ^{11}B nmr spectrum of this carborane (Figure 2a) reflects this symmetry by exhibiting four resonances with relative areas (from low field) of 2:2:4:2, assigned¹² to B(9,12), B(8,10), B(4,5,7,11), and B(3,6), respectively (all ^{11}B chemical shifts reported herein are relative to $BF_3 \cdot O(C_2H_5)_2$).

Figure 2

Figure 2 illustrates how the ^{11}B nmr spectrum of $1,2-C_2B_{10}H_{12}$ changes with increasing deuteration when the exchange is catalyzed by $(PPh_3)_3RuHCl$. It is clear that this catalyst introduces deuterium with definite stereoselectivity since the observed rates for incorporation at the four sets of sites are in the order $B(3,6) > B(4,5,7,11) > B(8,10) > B(9,12)$. This order is precisely the reverse of that established for electrophilic substitutions on $1,2-C_2B_{10}H_{12}$,¹³ which occur most readily at the boron atoms farthest removed from the relatively electropositive carbon atoms.¹⁴ Nucleophilic substitution reactions have not, to

our knowledge, been previously observed at boron-hydrogen bonds on $1,2\text{-C}_2\text{B}_{10}\text{H}_{12}$, but they would be expected to follow the sequence observed in the present case. Base degradation of the closo carborane to a nido species (eq. 2) is known to pro-



ceed by attack at those sites closest to the carbon atoms, B(3,6).¹³ Also, work by Klabunde and Parshall⁸ implicates nucleophilic attack in the oxidative addition of aromatic C-H bonds in the course of deuterium exchange on substituted benzenes catalyzed by polyhydride transition metal complexes. The mechanism of catalytic deuteration will be discussed later in more detail.

$1,7\text{-C}_2\text{B}_{10}\text{H}_{12}$. Figure 3 reveals that deuteration of $1,7\text{-C}_2\text{B}_{10}\text{H}_{12}$ as catalyzed by $(\text{PPh}_3)_3\text{RuHCl}$ is also highly stereoselective. Rates of deuterium incorporation are in the order $\text{B}(2,3) > \text{B}(4,6,8,11) > \text{B}(5,12) > \text{B}(9,10)$, based on the latest assignment of the ^{11}B nmr spectrum presented by Hart and Lipscomb.¹⁵ The previous analysis of this spectrum, by Stanko, *et al.*,¹⁶ differed by assignment of the lowest field resonance to B(9,10) and the one at next lowest field to B(5,12). Since electrophilic substitution is well established as occurring first at B(9,10),¹⁷ these should be the sites least susceptible to nucleophilic attack. Hence, the nucleophilic character of the deuterium exchange reaction and the observed order of exchange clearly support the ^{11}B nmr assignment of Hart and Lipscomb. Further support comes from recent work by Aufderheide and Sprecher¹⁸ on ^{11}B nmr shifts observed with halogenated carboranes.

Figure 3

$1,12\text{-C}_2\text{B}_{10}\text{H}_{12}$. Since all boron sites are equivalent in this species, no stereoselectivity is possible. However, the initial rate of deuteration

was considerably slower for this carborane than for any other studied.

1,6-C₂B₈H₁₀. Only two of the resonances in the ¹¹B nmr spectrum of this carborane have been assigned. The low field resonance of area 1 in the partially resolved 19.3 MHz spectrum of the 1,6-dimethyl derivative was assigned to the low coordinate boron atom, B(10).¹⁹ Therefore the remaining resonance of area 1 in the 80.53 MHz spectrum (Figure 4a) must be B(8). As the only boron atom in the carborane cage not adjacent to a carbon atom, B(8) might be expected to be the site least susceptible to nucleophilic attack. This was confirmed by the series of spectra in Figure 4. The remaining sites [B(2,3), B(4,5), B(7,9)] are deuterated at nondistinguishable rates under these conditions, but this may be due to a change in the rate determining step for exchange at these much more susceptible sites (vide infra).

Figure 4

Exchange with Carborane Substrates Catalyzed by Hydridometallocarboranes.

During the course of our investigation of (PPh₃)₃RuHCl-catalyzed deuterium exchange, a number of hydridometallocarboranes were synthesized. These complexes proved to be active catalysts for the hydrogenation, hydrosilylation, and the isomerization of olefins.²⁰ Examination of the effectiveness of 2,2-(PPh₃)₂-2-H-2,1,7-RhC₂B₉H₁₁, 3,3-(PPh₃)₂-3-H-3,1,2-RhC₂B₉H₁₁ and their iridium congeners as catalysts for deuterium exchange at B-H bonds revealed that they were much more active than (PPh₃)₃RuHCl. Table II gives the results for a series of exploratory deuteration reactions catalyzed by these species.

The catalysts recovered from these reactions had undergone deuterium exchange at B-H bonds as indicated by both their ir and ¹¹B nmr spectra. Unlike (PPh₃)₃RuHCl, these complexes do not undergo ortho metallation and hence, the ir spectra did not show bands for ortho deuterated triphenylphosphine ligands.

Also unlike $(PPh_3)_3RuHCl$, the catalysts, when recovered at intermediate stages of exchange with the substrates, were not perdeuterated at available sites on the catalyst. Instead, the extent of exchange at both B-H and M-H bonds in the catalyst was similar to that found for B-H bonds in the substrates as judged from the intensities of ν_{MH} , ν_{MD} , ν_{BH} , and ν_{BD} absorptions in the ir spectra.

The spectra in Figures 5 and 6 illustrate another difference in deuterium exchange when catalyzed by hydridometalloboranes. Little stereoselectivity was shown for incorporation of deuterium in $1,7-C_2B_{10}H_{12}$, and the small stereoselectivity observed appears to be in reverse order from that shown when the exchange was catalyzed by $(PPh_3)_3RuHCl$.

Figures 5 and 6

Among these hydridometalloborane catalysts, the $2,1,7-MC_2^{21}$ isomers were much more active than the $3,1,2-MC_2^{21}$ but the identity of the metal atom apparently made little difference. The activity of $3,1,2-IrC_2$ was essentially the same as that of $3,1,2-RhC_2$, and $2,1,7-IrC_2$ was slightly more active than $2,1,7-RhC_2$.

Exchange with Carborane Substrates Catalyzed by Other Species.

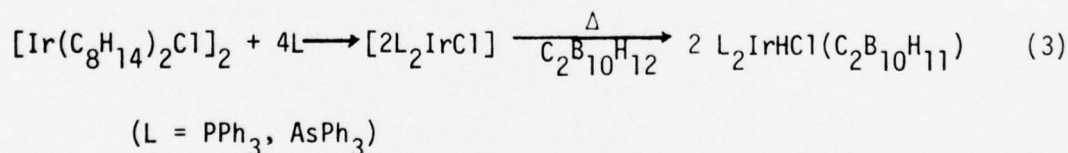
Table III lists the results of deuterium exchange catalyzed by other species. While $(PPh_3)_3RhCl$ is less active than $(PPh_3)_3RuHCl$ and also unstable under the reaction conditions, it showed the same stereoselectivity as $(PPh_3)_3RuHCl$. No stereoselectivity was shown by 10% Pd on C, which was also less active than $(PPh_3)_3RuHCl$. The products of systems 31 and 32 showed no trace of exchange at B-H but did exhibit deuterium exchange at carboranyl C-H.

$(PPh_3)_2(CO)IrCl$. Vaska's complex was found to be more active than $(PPh_3)_3RuHCl$ for exchange with $1,7-C_2B_{10}H_{12}$ (systems 33 and 34). The ^{11}B nmr spectra shown in Figure 7 revealed that the stereoselectivity of exchange catalyzed by this complex was intermediate between that of $(PPh_3)_3RuHCl$ and that of the hydridometallocarborane catalysts. Little preference between B(2,3), B(4,6,8,11), and B(5,12) sites was observed, but the exchange was distinctly slower at the B(9,10) sites.

Figure 7

The iridium-containing species isolated was identified as $(PPh_3)_2(CO)-IrD_2Cl$ by comparison of its ir spectrum with that of authentic material prepared from $(PPh_3)_2(CO)IrCl$ and D_2 .

L_2IrCl . We recently reported the synthesis of a number of stable B-σ-carboranyl iridium complexes by direct oxidative addition of carboranyl B-H bonds to L_2IrCl species prepared in situ according to eq. 3.²² One of these B-σ-carboranyl iridium complexes, $2-[(PPh_3)_2IrHCl]-1,7-C_2B_{10}H_{11}$, was tested



for catalytic activity in system 35. The activity of this complex was the greatest shown of all species tested; complete exchange of B-H for B-D in $1,7-C_2B_{10}H_{12}$ was obtained in less than 24 hr at 65° . The stereoselectivity of this exchange was similar to that found with $(PPh_3)_2(CO)IrCl$; the B(9,10) sites were the slowest to exchange and the others exchanged at nondistinguishable rates. Equivalent results were obtained with $(PPh_3)_2IrCl$, prepared in situ as described above. Figure 8 shows that complete deuteration could be achieved

even within 20 hrs at 40°. Figure 8 also shows that when AsPh₃ was used as the ligand exchange was slightly less rapid than that observed with PPh₃ and that the stereoselectivity became similar to that found with (PPh₃)₃RuHCl.

Figure 8

The catalyst residues from these reactions exhibited ν_{IrD} but not ν_{BH} or ν_{BD} bands and were not further characterized. It appears that the L₂IrCl species or hydrogen adducts thereof are probably the active catalysts and not the $\underline{\text{B}}-\sigma$ -carboranyl iridium complexes themselves.

Exchange with Other Substrates.

3-($\eta^5\text{-C}_5\text{H}_5$)-3,1,2-CoC₂B₉H₁₁. The low energy mass spectrum of 3-($\eta^5\text{-C}_5\text{H}_5$)-3,1,2-CoC₂B₉H₁₁, unlike that of carboranes,²³ fits the theoretical distribution²⁴ of molecular ions very closely, implying little hydrogen loss from the molecular ions under these conditions. This situation makes it possible to directly determine the average number of deuterium atoms per molecule by taking the difference between the mass average of the molecular ions of the product and that of the starting material, assuming equal ionization of all isotopic species. Table IV lists the mass

Table IV

spectrum of the undeuterated metallocarborane and of several deuterated products. From this data, the average number of deuterium atoms in the product of system 10 was estimated to be 6.8. However, further examination of the 70 eV mass spectrum revealed that isotopic exchange had also occurred in the cyclopentadienyl ligand. The intensities of the C₅H_{5-x}D_xCo⁺ ions are also given in Table IV and, when corrected for the isotopic distribution of ¹³C, they indicate

that the product of system 10 was 11% d_0 , 37% d_1 , and 52% d_2 in the cyclopentadienyl ligand (again assuming equal ionizations for all isotopic species). This is an average of 1.4 D per molecule not resident at boron, leaving an average of 5.4 D per molecule on the carborane cage. The relative absorbances of the grossly non-Lorentzian ν_{BH} and ν_{BD} absorptions implied 4.7 D per molecule, pointing out the error which may be inherent in the ir analysis of non-Lorentzian absorptions.

In an identical manner, the product of system 27b was found to have an average deuterium content of 6.2 D per molecule of which 0.12 D was present in the cyclopentadienyl ligand (89% d_0 , 9% d_1 , 1% d_2) leaving an average of 6.1 D per molecule at boron.

Figure 9 illustrates the stereoselectivity of exchange with this substrate.

Figure 9

The assignment of the ^{11}B nmr resonances is based on that for the nearly identical spectrum of the bis complex $[3,3'-Co(1,2-C_2B_9H_{11})_2]^-$.²⁵ The B(4,7) and B(9,12) resonances overlap and are not definitely assigned. However, electrophilic bromination of $[3,3'-Co(1,2-C_2B_9H_{11})_2]^-$ has been shown by X-ray crystallography to yield the 8,8',9,9',12,12'-hexabromo-complex.²⁶ Thus, for nucleophilic attack as postulated here for $(PPh_3)_3RuHCl$ catalyzed exchange, the B(8) and B(9,12) sites would be expected to be the last deuterated. The spectra in Figure 9, therefore, imply the following order for rates of deuterium exchange: $B(6) > B(5,11) > B(4,7), B(10) > B(8), B(9,12)$. Although the magnitude of the rates differ, their relative order is close to that observed for the parent carborane, $1,2-C_2B_{10}H_{12}$ (vide supra). The sites adjacent to the metal atom, which replaced B(3), are slightly inhibited relative to the sites which were symmetrically related in $1,2-C_2B_{10}H_{12}$. This inhibition may be due either to an electronic effect or to steric hindrance by the cyclopentadienyl

ligand. The small magnitude of the effect implies that replacement of a B-H vertex in the icosahedron by a $(\eta^5\text{-C}_5\text{H}_5)\text{Co}$ vertex causes no large change in the relative electron distribution in the cage. This observation is in accord with certain empirical and theoretical concepts of polyhedral bonding.²⁷⁻³¹

System 27 revealed a new characteristic in the catalytic behavior of the hydridometalloborane $2,2\text{-(PPh}_3)_2\text{-2-H-2,1,7-RhC}_2\text{B}_9\text{H}_{11}$. Although the more active sites of the metalloborane substrate were rapidly deuterated at nearly identical rates (as was found with the carborane substrates) the rather inactive sites B(8) and B(9,12) were deuterated much more slowly. Thus, for sufficiently inactive sites, the hydridometalloborane catalyst also effects stereoselective deuteration (cf. Figure 9e).

$1\text{-(}\eta^5\text{-C}_5\text{H}_5\text{)-1,2,4-CoC}_2\text{B}_8\text{H}_{10}$. The product of system 12 was analyzed by mass spectroscopy in the manner described for $3\text{-(}\eta^5\text{-C}_5\text{H}_5\text{)-3,1,2-CoC}_2\text{B}_9\text{H}_{11}$. The results indicated an average of 6.1 deuterium atoms per molecule of which 0.08 D was present in the cyclopentadienyl ligand (93% d_0 , 6% d_1 , 1% d_2). The ^{11}B nmr spectrum consisted only of singlets, implying little if any stereoselectivity at this stage of deuteration. Although it might appear at earlier stages of exchange or at lower temperatures, the lack of stereoselectivity could reflect a change in the rate determining step for this highly susceptible substrate (*vide infra*).

$\text{B}_{10}\text{H}_{14}$. Decaborane(14) reacted with $(\text{PPh}_3)_3\text{RuHCl}$ under the conditions of system 13 with evolution of H_2 and formation of a brown precipitate (not characterized). The resulting mixture was still active for the partial catalytic deuteration of $\text{B}_{10}\text{H}_{14}$ as shown by the ir and ^{11}B nmr spectra of the product of system 13. With the more active catalyst $2,2\text{-(PPh}_3)_2\text{-2-H-2,1,7-RhC}_2\text{B}_9\text{H}_{11}$ under the conditions of system 30, more extensive deuteration occurred. Catalyst decomposition also accompanied this reaction, albeit more slowly than with $(\text{PPh}_3)_3\text{-RuHCl}$. Exchange apparently does not occur with the bridge hydrogens since the ir spectra of these products showed no evidence for ν_{BDB} , expected in the 1300-

1400 cm^{-1} region.³²

Figure 10 shows the ^{11}B nmr spectra of $\text{B}_{10}\text{H}_{14}$ and the deuterated products.

Figure 10

The assignment of the resonances is based on those reviewed by Eaton and Lipscomb.³³ From these spectra it is clear that the order of rates for deuterium exchange at sites in $\text{B}_{10}\text{H}_{14}$ is $\text{B}(6,9) > \text{B}(5,7,8,10) > \text{B}(2,4) > \text{B}(1,3)$. The order predicted for nucleophilic substitution from theoretical studies of $\text{B}_{10}\text{H}_{14}$ differed by predicting $\text{B}(1,3) > \text{B}(2,4)$.³⁴ The partial order $\text{B}(6,9) > \text{B}(5,7,8,10)$ has been experimentally confirmed,³⁵ but to our knowledge, no nucleophilic substitution has heretofore been reported to have occurred at $\text{B}(1,3)$ or $\text{B}(2,4)$. Although electrophilic halogenation showed the substitution order $\text{B}(2,4) > \text{B}(1,3)$,³⁶ the preference was slight and electrophilic deuteration showed no discernable preference between these two sites.³⁷ Thus, either the theoretical predictions for nucleophilic substitution of $\text{B}_{10}\text{H}_{14}$ need further refinement or some electronic effect peculiar to the transition state for transition metal catalyzed deuteration has reversed the normal reactivity for these sites.

$(\text{CH}_3)_3\text{NBH}_3$. The ^{11}B nmr spectrum of $(\text{CH}_3)_3\text{NBH}_3$ is a 1:3:3:1 quartet. The product of system 14 had an ^{11}B nmr spectrum exhibiting only a singlet, implying complete exchange for the hydrogen atoms on boron. The ir spectrum confirmed that there had been >90% deuteration at boron and gave no evidence for exchange in the methyl groups.

Comparison of Reactivities in Icosahedral Substrates.

A qualitative comparison of the reactivity of various sites for exchange under identical conditions is shown in Figure 11. These ^{11}B nmr spectra clearly

Figure 11

show that the B(3,6) sites in $1,2-C_2B_{10}H_{12}$ are the most susceptible of any in the four substrates displayed. The other sites adjacent to two carbon atoms, B(6) in $3-(\eta^5-C_5H_5)-3,1,2-CoC_2B_9H_{11}$ and B(2,3) in $1,7-C_2B_{10}H_{12}$, also show high reactivity. The B(6) site in the metallocarborane is apparently deactivated with respect to the equivalent site in parent $1,2-C_2B_{10}H_{12}$, but the B(5,11) sites are apparently activated. All of the sites adjacent to only one carbon atom show moderate reactivity, the B(5,12) sites in $1,7-C_2B_{10}H_{12}$ and B(2-11) sites in $1,12-C_2B_{10}H_{12}$ showing about equal reactivity. None of the sites nonadjacent to carbon atoms showed any reactivity under these conditions.

Effect of Oxygen on Hydridometallocarborane Catalysts.

When this work was first communicated,² the results of several exchange reactions, including systems 15 and 16, showing very rapid and complete deuteration of carboranes at 65° , were reported. Subsequently, it was learned that these rapid deuteration reactions depended upon the residual oxygen found in the deuterium gas which had been used as received. Thereafter, all deuterium gas was deoxygenated before use and tables I-III indicate which reactions were carried out with purified deuterium. The rate enhancement caused by minute quantities of oxygen is apparent in the greatly reduced conversions with these same catalysts and $1,7-C_2B_{10}H_{12}$ in the absence of O_2 and also by the subsequent rate enhancement observed in systems 20, 21, and 24 upon exposure to air (cf. Table II and Figures 5 and 6). The removal of oxygen from the deuterium gas supply did not have any noticeable effect on exchange reactions catalyzed by $(PPh_3)_3RuHCl$.

Effect of Excess Triphenylphosphine on Various Catalysts.

In an experiment identical to that described by system 21, except for the addition of 0.05 mmol PPh_3 to the reaction mixture, the deuteration of $1,7-C_2B_{10}H_{12}$ catalyzed by $2,2-(PPh_3)_2-2-H-2,1,7-RhC_2B_9H_{11}$ was completely inhibited. Both catalyst and substrate were recovered unchanged.

Deuterium exchange catalyzed by $(PPh_3)_2(CO)IrCl$ was almost as completely inhibited by 0.05 mmol PPh_3 in an experiment otherwise identical to system 39. After 48 hrs at 100^0 , deuteration was only barely detectable and much less exchange had occurred than after only 1 hr without the excess phosphine.

Deuterium exchange catalyzed by $(PPh_3)_3RuHCl$ was apparently unaffected by excess PPh_3 . Similar insensitivity to added phosphine was found for the ortho deuteration reaction of this catalyst.⁶

Deuterium Scrambling Experiment

Figure 12 illustrates the relative rates of deuterium exchange and deuterium

Figure 12

scrambling of $1,7-C_2B_{10}H_{12}$ as catalyzed by $2,2-(PPh_3)_2-2-H-2,1,7-IrC_2B_9H_{11}$. Spectrum a is that of undeuterated $1,7-C_2B_{10}H_{12}$ and spectrum e is that of $1,7-C_2B_{10}H_{12}$ selectively deuterated at the B(2,3) positions (approx. dl). The spectra below a (b-d) show deuterium uptake in the presence of D_2 while the spectra below e (f-h) show the scrambling of deuterium from B(2,3) to other positions in the cage in the absence of D_2 . These data imply that under equivalent experimental conditions, scrambling of deuterium occurs at least as fast as deuterium incorporation.

Discussion

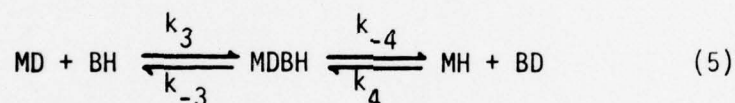
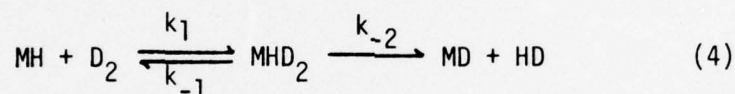
Perhaps the most noteworthy result of the catalytic exchange experiments is the striking difference in stereoselectivity between various catalysts. Some, most notably $(PPh_3)_3RuHCl$, show a well-defined stereoselectivity implying nucleophilic character for the attacking metal species, while others, especially the hydridometallocarborane catalysts, show almost no stereoselectivity with some substrates. Other catalysts, such as $(PPh_3)_2(CO)IrCl$ and L_2IrCl species, show intermediate stereoselectivities. Any proposed general mechanism for transition metal catalyzed deuterium exchange at boron-hydrogen bonds must be capable of

explaining these diverse reactivities.

To simplify discussion, the general scheme proposed below is based on a metal hydride species as the active catalyst. Most of the complexes studied were metal hydrides to begin with, while those that were not readily form such species in the presence of hydrogen. The specific nature of the active catalyst formed from those complexes which were studied will be discussed in the appropriate section for each catalyst.

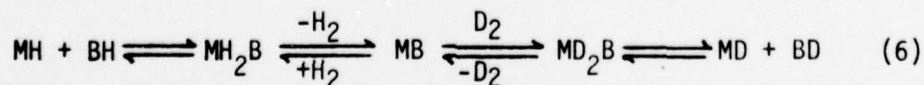
General Mechanism

The oxidative addition and reductive elimination scheme given in eqs. 4 and 5 are adequate to explain the results reported above with the exception



that, depending on the nature of the active catalyst, dissociation or association of neutral ligands may occur in addition to the oxidative addition or reductive elimination steps (this point will be discussed further in later sections). Reactions involving oxidative addition of H_2 or HD need not be considered as these species were present only in very low concentrations relative to D_2 .

Although the reactions in eq. 6 are also a possible process for the intro-



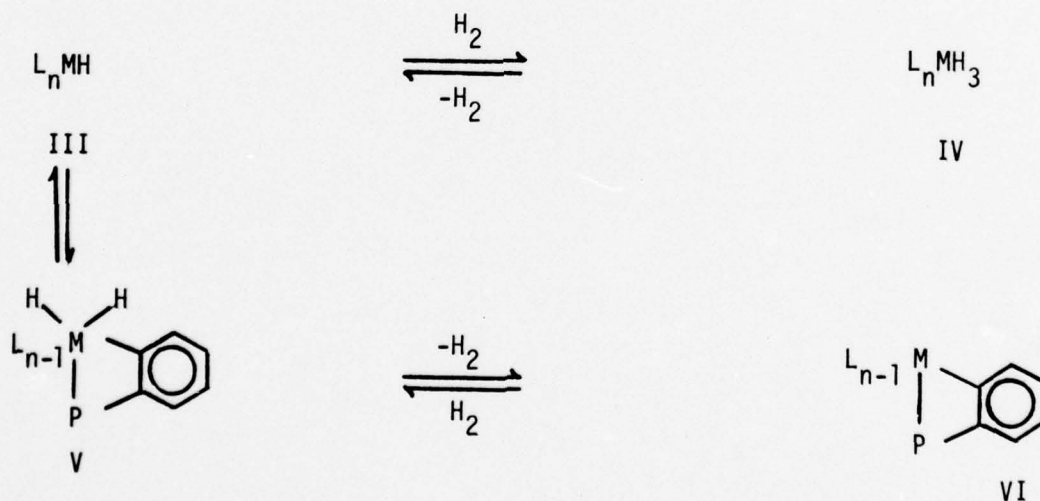
duction of deuterium into the catalytic system, experiments with $(\text{PPh}_3)_3\text{RuHCl}$ and the hydridometallocarborane catalysts have shown that no MB species accumulate in the absence of D_2 . Such accumulation might be expected based on eq. 6.

For these particular catalysts, with which most of the mechanism studies have been carried out, this is not a viable exchange process. For other catalysts, the possible role of reactions such as eq. 6 will be discussed in the appropriate section.

Catalysis by $(PPh_3)_3RuHCl$.

The most significant result of exchange catalyzed by $(PPh_3)_3RuHCl$ was the stereoselectivity shown for deuterium incorporation at chemically nonequivalent sites within the substrates. However, before the requirements for this stereoselectivity can be discussed, it is necessary to explore the nature of the intermediates in eqs. 4 and 5.

As mentioned earlier, $(PPh_3)_3RuHCl$ is known to exchange 19 hydrogen atoms for deuterium when heated with D_2 . The general mechanism postulated⁶ for ortho phenyl C-H exchange (shown below) allowed two possible processes for the



introduction of deuterium, $III \rightleftharpoons IV$ and $V \rightleftharpoons VI$. However, the stability of $(PPh_3)_3RuHCl$ solutions in the absence of hydrogen or deuterium rules out $V \rightleftharpoons VI$ as a viable path for this particular catalyst. Ortho metalated species such as VI or decomposition products thereof would be expected to

accumulate if that path were available. The remaining process, $\text{III} \rightleftharpoons \text{IV}$, is the equivalent of eq. 4. Since the addition of excess PPh_3 did not inhibit ortho deuteration of PPh_3 or deuterium exchange with carboranes, ligand dissociation is not a part of the exchange process. Hence, for this catalyst, MH in the scheme is most probably $(\text{PPh}_3)_3\text{RuHCl}$ itself.

Since the catalyst is recovered unchanged except for self-deuteration, the equilibria must favor this species and not MH_3 or MH_2B type species. Thus the steady-state approximation may be applied to the concentration of MH_3 and MH_2B for initial rate calculations.

To rationalize the stereochemistry of the exchange reactions, two assumptions must be made. The first is that the attack of catalyst at a B-H bond (k_3) is nucleophilic in character. From this it follows that the magnitude of k_3 for attack at various sites in the substrate will vary with the susceptibility of each site towards such nucleophilic attack. If $k_3(1)$ is defined as the particular k_3 for attack at the most susceptible set of sites, BH(1), while $k_3(2)$ as that for attack at the next susceptible set, BH(2), etc., then $k_3(1) > k_3(2) > \dots k_3(n)$.

The second general requirement for stereoselectivity is that $k_1 > k_4(1)$. This follows from inspection of the relevant equilibria in the scheme. In the case where this requirement is not met, eq. 5 provides a path for attainment of the thermodynamic distribution of deuterium among all those sites for which oxidative addition of a B-D bond is more facile than oxidative addition of deuterium to the catalyst, i.e., for which $k_4 > k_1$.

If $k_1 \gg k_4(1) \gg k_4(2)$, the simplest case, the rate-determining step will be the reaction whose rate constant is $k_3(1)$. In this case, after a short period of rapid exchange, during which almost all MH is converted to MD, the initial

rate equation for deuteration of the most active site will become

$$\frac{d[\text{BD}(1)]}{dt} = k_3(1) \left[\frac{k_{-4}(1)}{k_{-3}(1)} \right] [\text{MD}][\text{BH}(1)] \quad (7)$$

Since no dependence of the rate on PPh_3 concentration was found, ligand dissociation is not involved and it is permissible to assume $[\text{MD}] = [\text{Ru}]_{\text{total}}$.

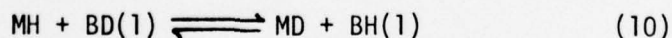
The observed initial rate equation would be

$$\frac{d[\text{BD}(1)]}{dt} = k_{\text{obs}}[\text{BH}(1)] \quad (8)$$

where

$$k_{\text{obs}} = k_3(1) \left[\frac{k_{-4}(1)}{k_{-3}(1)} \right] [\text{Ru}]_{\text{total}} \quad (9)$$

The other simple case for stereoselective exchange, $k_4(1) \gg k_1 \gg k_4(2)$, would have the reaction whose rate constant is k_1 as the rate-determining step for deuteration of $\text{BH}(1)$. For this situation, the equilibria in eq. 5 are fast relative to the rate-determining step and maintain the following equilibrium between MH and MD :



The equilibrium constant for eq. 10 should be near 1. In this case there is no rapid prior exchange with catalyst, so the initial rate equation would have the form

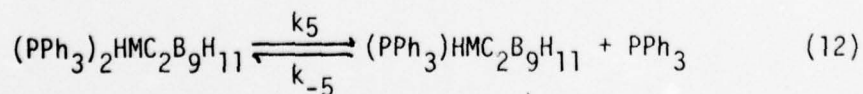
$$\frac{d([\text{BD}(1)] + [\text{MD}])}{dt} = k_1 \left[\frac{k_{-2}}{k_{-1}} \right] [\text{Ru}]_{\text{total}} P_{\text{D}_2} \quad (11)$$

The fraction exchange at the hydride (and ortho phenyl hydrogens) of the catalyst would parallel, according to eq. 10, that at the active site of the substrate.

Preliminary kinetic experiments¹ with $(PPh_3)_3RuHCl$ as catalyst indicate that the correct ordering of rates for this catalyst is $k_1 > k_4(1) \gg k_4(2)$, at least for substrates with sites no more active than B(3,6) on $1,2-C_2B_{10}H_{12}$. This conclusion follows from the observation of an initial, rapid exchange of the 19 exchangeable sites of the catalyst before a significant fraction of the substrate had undergone exchange. If this proposed mechanism is correct, the initial rate should be found to depend on catalyst and substrate concentrations but not on P_{D_2} (except during the catalyst self-exchange period), and the observed initial rate should have the form of eq. 8 after the catalyst self-exchange period.

Catalysis by Hydridometallocarboranes.

The stereochemical results of deuterium exchange catalyzed by the hydrido-metallocarboranes, which are greatly at variance with those for $(PPh_3)_3RuHCl$, may also be rationalized by the scheme in eqs. 4 and 5 if certain requirements are met. The nature of the MH active catalysts for these species is not completely defined, but they are probably not the parent hydridometallocarborane. Since one equivalent of excess PPh_3 completely inhibits exchange at both the metal hydride and substrate B-H bonds, it is most likely that MH is formed with accompanying ligand dissociation:



It has been suggested that $(PPh_3)HMC_2B_9H_{11}$ has undergone an internal redox reaction from a formal M(III) to a formal M(I) species more accurately represented as $(PPh_3)MC_2B_9H_{12}$.³⁸ Oxidative addition reactions k_1 and k_3 are easier

to rationalize for low coordinate Rh^{I} or Ir^{I} than for Rh^{III} or Ir^{III} species,^{5b,39-41} although Ir^{V} species have been postulated in homogeneous hydrogenation mechanisms.⁴¹

The tremendous enhancement of rate for hydridometallocarborane catalysts when treated with minute amounts of oxygen may reflect the unfavorable nature of the K_5 equilibrium in eq. 12. If the oxygen used to make Ph_3PO , the equilibrium shifts towards the presumed MH active catalyst. If dissociation is very unfavorable in the absence of oxygen then even very small quantities of oxygen could result in huge relative increases in the concentration of MH active catalyst. A similar effect of oxygen in $(\text{PPh}_3)_3\text{RhCl}$ catalyzed homogenous hydrogenation has also been discussed in these terms, but an oxidized catalyst was not ruled out⁴¹ and cannot be excluded in the present study. Indeed, a purple metallocarborane complex could be isolated from oxidized catalytic solutions of $3,3-(\text{PPh}_3)_2-3\text{-H-3,1,2-RhC}_2\text{B}_9\text{H}_{11}$, but it has not been fully characterized. It is clear that further study is needed to define more precisely the role of oxygen in rate enhancement.

The stereochemical results with this catalyst are easily rationalized if $k_4(i) > k_1$, where $k_4(i)$ is the rate constant appropriate to the least active site in the substrate for which nonselective deuteration is observed. In this case the equilibria in eq. 5 provide an effective path, similar to eq. 10, for attainment of the thermodynamic rather than kinetic distribution of deuterium among those sites for which $k_4 > k_4(i)$.

The presence of fast equilibria such as eq. 10 is also supported by the previously noted observation that exchange of D on the metal parallels that on boron, regardless of the relative quantities of catalyst and substrate, the nature of substrate, or of the time and temperature of exchange. More direct evidence is given in Figure 12 where a partially, stereospecifically

deuterated carborane is shown to undergo scrambling faster than exchange under the same conditions.

Given that the equilibria in eq. 5 do establish the thermodynamic distribution of deuterium, the spectra in Figures 5 and 6 imply that the thermodynamic preference is the opposite of the kinetic.

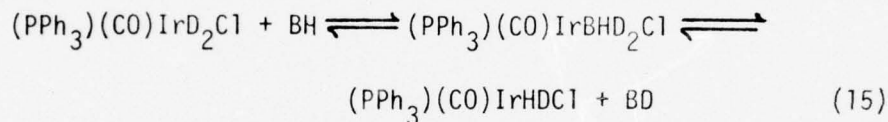
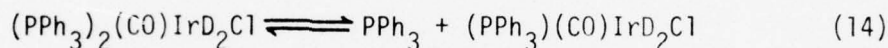
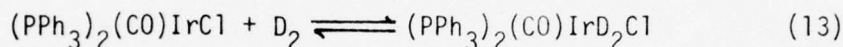
The greater effect of oxygen on the rate of 3,1,2-MC₂ congeners suggests that the large difference between their rates and those of the 2,1,7-MC₂ isomers may be due to differences in K₅ rather than in k₁.

An alternate mechanism for the hydridometalloborane catalysts, which might be proposed on the basis of the lack of stereoselectivity, is that the k₃ step for these catalysts is no longer a nucleophilic attack, but is perhaps free radical in nature. This may be consistent with the results obtained with carborane substrates, but does not explain the partial stereoselectivity obtained with 3-(n⁵-C₅H₅)-3,1,2-CoC₂B₉H₁₁ and B₁₀H₁₄ substrates. The mechanism proposed herein, however, is still consistent since the sites which exchange more slowly are the least susceptible to nucleophilic attack, and could show selectivity because k₃ for these sites is smaller than k₁.

Catalysis by (PPh₃)₂(CO)IrCl.

Exchange catalyzed by (PPh₃)₂(CO)IrCl showed activity similar to that of the hydridometalloboranes; observed rates were faster than the 3,1,2-MC₂ congeners (without oxygen) but slower than the 2,1,7-MC₂ species. The stereoselectivity was intermediate between that of (PPh₃)₃RuHCl and the hydridometalloboranes, showing selectivity only at the least active sites in 1,7-C₂B₁₀H₁₁, B(8,10). In general terms, this stereoselectivity requires the active catalytic species to oxidatively add BH faster than D₂ for all sites except B(8,10), for which oxidative addition of BH becomes rate-determining.

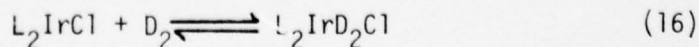
The recovered iridium-containing species was identified as $(\text{PPh}_3)_2(\text{CO})\text{IrD}_2\text{Cl}$. Although this is an MD type species, it is also a six-coordinate Ir^{III} complex to which further oxidative additions seem unlikely. However, the role of $\text{L}_2(\text{CO})\text{IrX}$ complexes in homogeneous hydrogenation has been widely studied⁴¹ and both eight-coordinate Ir^{V} and lower coordinate Ir^{V} species have been postulated. The inhibitory effect of added PPh_3 implicates dissociation of PPh_3 in the formation of the active catalyst. Thus, $(\text{PPh}_3)(\text{CO})\text{IrD}_2\text{Cl}$ might be a reasonable candidate. A suitable scheme for deuterium exchange by this catalyst could be based on the following equilibria:

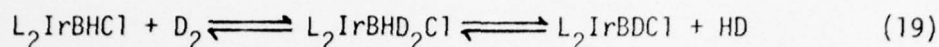
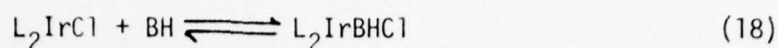
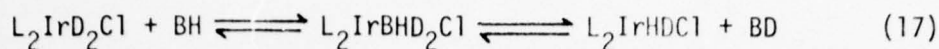


However, since L_2IrCl species are also active catalysts for deuterium exchange, an equally suitable scheme could be based on eq. 16-19 with $(\text{PPh}_3)(\text{CO})\text{IrCl}$ as the L_2IrCl species. The evidence is insufficient for valid conclusions to be made.

Catalysis by L_2IrCl Species.

These complexes were by far the most active catalysts studied. The dependence of stereoselectivity on the identity of L indicates that the relative facility of oxidative additions of D_2 or BH depends on the environment of the metal atom. A possible scheme for deuterium exchange catalyzed by these species could be based on some or all of the following equilibria:





The reaction in eq. 18 has been observed in the absence of deuterium²² and the $(L_2IrHCl)C_2B_{10}H_{11}$ species used for systems 35 and 37 were prepared in this manner. Eq. 19 is an equilibrium similar to eq. 6.

Conclusion

Catalysis of deuterium exchange with terminal boron-hydrogen bonds by transition metal containing species is apparently a facile and general reaction. The evidence presented herein implies that during oxidative addition of the B-H bond, the metal attacks the boron in a nucleophilic reaction. The observed stereospecificity of deuterium exchange may reflect the reactivity of the various sites in the substrate towards nucleophilic attack. The stereoselectivity may also reflect the thermodynamic distribution at those sites if deuterium exchange with the catalyst is slower than attack of the catalyst at some or all substrate sites.

The most generally useful catalysts for synthesis of deuterated boranes, carboranes, and metallocarboranes appear to be the readily available $(PPh_3)_3RuHCl$ and L_2IrCl complexes. Partially, stereoselectively deuterated species can be prepared by use of either $(PPh_3)_3RuHCl$ or $(AsPh_3)_2IrCl$ as the catalyst. Completely deuterated species are most easily prepared with the most active catalyst, $(PPh_3)_2IrCl$.

The stereoselective deuteration promises to be useful for assignment of ^{11}B nmr spectra when the resonances are sufficiently well resolved and a prediction of relative reactivity for the various sites can be made on either theoretical or empirical grounds. One empirical rule evident from this study

is that boron atoms adjacent to two carbon atoms are more reactive towards nucleophilic substitution than those adjacent to only one carbon atom, and those adjacent to no carbon atoms are the least reactive. Within these groups more subtle factors determine the relative reactivities.

Experimental

Unless otherwise noted, all reactions were carried out under an atmosphere of dry, oxygen-free nitrogen and solvents were saturated with nitrogen prior to use.

Physical Measurements. Infrared spectra of KBr pellets or Nujol mulls were recorded on a Perkin-Elmer 137 sodium chloride spectrophotometer. Proton nmr spectra were obtained at 251 MHz and ^{11}B nmr spectra at 80.53 MHz on a superconducting, Fourier-transform instrument designed and constructed by Professor F. A. L. Anet and coworkers of this department. Mass spectra were obtained with an Associated Electrical Industries MS-9 spectrometer. Elemental analyses were carried out by the Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

Materials. Reagent grade benzene and toluene were distilled from CaH_2 and stored under nitrogen. Dichloromethane and carbon tetrachloride were reagent grade. Decaborane(14), $1,2\text{-C}_2\text{B}_{10}\text{H}_{12}$ and $1,7\text{-C}_2\text{B}_{10}\text{H}_{12}$ were sublimed prior to use. $1,12\text{-C}_2\text{B}_{10}\text{H}_{12}$ ⁴² was purified by chromatography with 30-60° petroleum ether on basic alumina according to the suggestion of Sieckhaus, et al.⁴³ Analysis by glc showed the recrystallized product to contain less than 0.01% $1,7\text{-C}_2\text{B}_{10}\text{H}_{12}$. $(\text{CH}_3)_3\text{NBH}_3$ was used as received from Matheson, Coleman and Bell. $1,6\text{-C}_2\text{B}_8\text{H}_{10}$,⁴² $3\text{-(}\eta^5\text{-C}_5\text{H}_5\text{)-3,1,2-CoC}_2\text{B}_9\text{H}_{11}$,⁴⁴ and $1\text{-(}\eta^5\text{-C}_5\text{H}_5\text{)-1,2,4-CoC}_2\text{B}_8\text{H}_{10}$ ⁴⁵ were prepared by literature methods.

$(PPh_3)_3RuHCl \cdot C_6H_5CH_3$ was prepared by the method of Schunn and Wonchoba.⁹ The hydridometallocarborane catalysts $3,3-(PPh_3)_2-3-H-3,1,2-MC_2B_9H_{11}$ ($M = Rh, Ir$) and $2,2-(PPh_3)_2-2-H-2,1,7-MC_2B_9H_{11}$ ($M = Rh, Ir$) were prepared by methods of Paxson and Hawthorne.^{20,38} $(PPh_3)_2(CO)IrCl$ was prepared by treating a benzene solution of PPh_3 and $[Ir(C_8H_{14})_2Cl]_2$ (4:1) with excess CO and crystallizing the product by addition of hexane. The preparation of $3-[(PPh_3)_2IrHCl]-1,7-C_2B_9H_{11}$ has been described.²²

Deuterium gas (99.7%) was obtained from Liquid Carbonic and was used as received for the early work described herein. When it was discovered that the residual oxygen in the gas was greatly enhancing the rate for the hydrido-metallocarborane catalysts, the gas was thereafter purified by passage through a column of Dow BTS catalyst (prepared with D_2) at 120° followed by passage through a column of Drierite.

$(PPh_3)(1-P(CH_3)_2-1,2-C_2B_{10}H_{11})_2RuHCl$ (II). A mixture of $(PPh_3)_3RuHCl \cdot C_6H_5CH_3$ (0.5 g, 0.5 mmol) and I, $1-P(CH_3)_2-1,2-C_2B_{10}H_{11}$ (0.5 g, 2.5 mmol), was heated to reflux in 15 ml of toluene. The purple solution rapidly turned red-orange and upon cooling a yellow-orange powder precipitated from the solution. This was collected by filtration, washed with ether and vacuum dried to yield 0.192 g of II. Addition of 25 ml ether to the filtrate precipitated another 0.066 g. Total yield was 64% of theoretical. The yellow-orange powder is air stable in the solid state for hours, but solutions rapidly turn green in air. Mp $227-230^\circ$ (dec). Anal. Calcd for $C_{26}H_{50}B_{20}P_3ClRu$: C, 38.63; H, 6.23; B, 26.75; P, 11.49; Cl, 4.38; Ru, 12.50. Found: C, 38.28; H, 6.24; B, 25.11; P, 11.59; Cl, 6.91; Ru, 12.55.

Deuterium Exchange Technique. The reactors consisted of 25 ml 3-necked flasks equipped with a reflux condenser connected to a nitrogen atmosphere, a magnetic stir bar, and a deuterium gas inlet tube which extended to near the bottom of the flask. The reactor was evacuated, filled with nitrogen, and the

substrate, catalyst and solvent introduced in a countercurrent of nitrogen. The reactor was brought to the desired temperature in an oil bath controlled to $\pm 1^\circ$ with a Therm-O-Watch regulator, and stirred at that temperature until the catalyst and substrate dissolved. Deuterium gas was then bubbled through the vigorously stirred solution at ca. 3 cc/min. The reactions were sampled at desired intervals by taking 1 or 2 ml aliquots by pipet in a countercurrent of nitrogen and treating them as described below.

Isolation of Substrates. Isolation of deuterated I was effected by chromatography of the product solution on silica gel with hexane/ CH_2Cl_2 . The phosphine containing fraction was stripped of solvent on a vacuum line.

The $\text{C}_2\text{B}_{10}\text{H}_{12}$ carboranes were isolated by transferring 2 ml aliquots to a sublimator, removing the solvent in vacuo, and subliming the product to a 0° cold finger. In later experiments, a 1 ml aliquot was filtered directly into an nmr tube through a 3 cm column of neutral alumina in a disposable pipet. Sufficient carborane for ir and mass spectral analysis could then be obtained by washing the column with 1 ml of CH_2Cl_2 and evaporating the solvent. All catalysts were retained by the alumina under these conditions. At the end of the reaction, the solution was cooled and the carborane was collected by sublimation as before. The catalyst residue from the sublimation was examined by ir spectroscopy after recrystallization from benzene/hexane.

Decaborane(14) and $(\text{CH}_3)_3\text{NBH}_3$ substrates were also isolated by the sublimation technique, but 1,6- $\text{C}_2\text{B}_8\text{H}_{10}$ proved to be too volatile and was isolated by preparative glc of a solution filtered through silica gel to remove the catalyst.

The metallocarborane substrates were isolated by chromatography of aliquots or of the product solution on silica gel with dichloromethane/hexane eluant. Rotary evaporation of the solvent from the metallocarborane fraction gave crystalline products in high yields.

Analysis for Deuterium Content. The metallocarborane substrates gave mass spectra at 14-16 eV which exhibited distributions of molecular ions close ($\pm 10\%$) to the calculated isotopic distributions.²⁴ Their deuterium content could be calculated, therefore, from the difference between the mass average of the molecular ions before and after deuteration (Table IV). The deuterium content in the cyclopentadienyl ligand was readily determined from isotopic analysis of the pattern of $[C_5H_{5-x}D_xCo]^+$ fragments in the 70 eV mass spectrum. This number of deuterium atoms was subtracted from the total to give the average number of deuterium atoms bonded to boron atoms in the product. The estimated error in this method is ± 0.2 D.

The mass spectra of carboranes, unfortunately, show extensive hydrogen loss even at low eV.²³ Therefore, the deuterium content of all substrates but the metallocarboranes was determined from infrared analysis. The relative amounts of B-H and B-D in these compounds was determined from comparison of the relative absorbances of ν_{BH} and ν_{BD} absorptions in their ir spectra (Nujol mull or KBr pellet) with those in spectra of standard mixtures of 1,12- $C_2B_{10}H_{12}$ and 1,12- $C_2H_2B_{10}D_{10}$. The assumptions inherent in this analysis are that the relative extinction coefficients of ν_{BH} and ν_{BD} are the same for all substrates, for all sites within a substrate, and at all degrees of deuteration of the substrate. The error in this analysis is estimated at ± 1 D but may be greater or less depending on the validity of the assumptions. The errors are greatest for those substrates with obviously non-Lorentzian absorptions, which includes all substrates but the carboranes.

The infrared analysis was modified, if necessary, upon examination of the ^{11}B nmr spectra. Where sufficiently well resolved, the resonances could be analyzed as overlapping singlets and doublets reflecting the relative concentration of D and H at that boron atom.

Acknowledgements.

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TABLE I

Conditions for and Results of Selected Deuterium Exchange
Reactions Catalyzed by $(\text{PPh}_3)_3\text{RuHCl}$

System	Substrate	mmol Substrate	mmol $(\text{PPh}_3)_3\text{RuHCl}$	Conditions ^a	Av # D in Product ^b
1a ~	1,2- $\text{C}_2\text{B}_{10}\text{H}_{12}$	2.0	0.20	3 days	6
b ~				5 days	7
2 ~		1.4	0.10	18 hr, 80°	5
3 ~		3.5	0.10	2 days	4
4 ~		1.0	0.05	2 hr ^c	2
5 ~	1,7- $\text{C}_2\text{B}_{10}\text{H}_{12}$	2.0	0.10	3 days	9
6a ~		1.0	0.05	15 hr, 80°	2
b ~				a + 6 hr, 100°	5
7 ~	1,12- $\text{C}_2\text{B}_{10}\text{H}_{12}$	1.0	0.05	20 hr ^c	2
8 ~	1,6- $\text{C}_2\text{B}_8\text{H}_{10}$	1.0	0.05	20 hr, 80°	7
9 ~		1.0	0.05	1 day	8
10 ~	3-($\eta^5\text{-C}_5\text{H}_5$)-3,1,2- $\text{CoC}_2\text{B}_9\text{H}_{11}$	1.0	0.10	3 days	5.4 ^d
11 ~		1.0	0.05	20 hr	3

TABLE I (cont)

System	Substrate	mmol Substrate	mmol (PPh ₃) ₃ RuHCl	Conditions ^a	Av # D in Product ^b
12 ~	1-(η^5 -C ₅ H ₅)-1,2,4- CoC ₂ B ₈ H ₁₀	2.0	0.10	18 hr, 80°	6.0 ^d
13a ^e ~	B ₁₀ H ₁₄	2.0	0.10	1 day	2
b ^e ~				3 days	3
14 ^e ~	(CH ₃) ₃ NBH ₃	4.0	0.05	1 day	3

a. Except where noted, reactions were at 100° in 20 ml toluene with D₂ bubbling at ca 3 cc/min and with rapid stirring.

b. Estimated from ir, ¹¹B nmr, and mass spectra.

c. Deuterium purified with BTS.

d. Deuterium also found in cyclopentadienyl ligand (see text).

e. Reaction was observed with catalyst.

TABLE II
Conditions for and Results of Selected Deuterium Exchange
Reactions Catalyzed by Hydridometallocarboranes

System	Substrate ^a	Catalyst ^b	Conditions ^c	Av # D in Product ^d
15 ~	1,2-C ₂ B ₁₀ H ₁₂	3,3-(PPh ₃) ₂ -3-H-3,1,2- RhC ₂ B ₉ H ₁₁ (0.027 mmol)	1 day, 65°e	10
16 ~		2,2-(PPh ₃) ₂ -2-H-2,1,7- RhC ₂ B ₉ H ₁₁ (0.027 mmol)	1 day, 65°e	10
17a ~		2,2-(PPh ₃) ₂ -2-H-2,1,7- IrC ₂ B ₉ H ₁₁	4 hr, 100°e	5
b ~			36 hr, 100°e	10
18 ~		3,3-(PPh ₃) ₂ -3-H-3,1,2- RhC ₂ B ₉ H ₁₁	1 hr, 100° then 6 hr, 65°	6
19a ~	1,7-C ₂ B ₁₀ H ₁₂	3,3-(PPh ₃) ₂ -3-H-3,1,2- RhC ₂ B ₉ H ₁₁	4 hr, 65°	trace
b ~			24 hr, 65° then 20 hr, 100°	5
20a ~			4 hr, 65°	trace
b ~			20 hr, 65°	1

TABLE II (cont)

System	Substrate ^a	Catalyst ^b	Conditions ^c	Av # D in Product ^d
c			b + O ₂ , 8 hr, 65° ^f	2
d			c + air, 14 hr, 65° ^g	5
21a		2,2-(PPh ₃) ₂ -2-H-2,1,7-	4 hr, 65°	1
		RhC ₂ B ₉ H ₁₁		
b			20 hr, 65°	6
c			+ air, 14 hr, 65° ^g	10
22a		3,3-(PPh ₃) ₂ -3-H-3,1,2-	4 hr, 65°	trace
		IrC ₂ B ₉ H ₁₁		
b			24 hr, 65° then	
			20 hr, 100°	5
23a			4 hr, 65°	3
		2,2-(PPh ₃) ₂ -2-H-2,1,7-		
		IrC ₂ B ₉ H ₁₁		
b			24 hr, 65° then	
			20 hr, 100°	10
24a			4 hr, 65°	3
b			20 hr, 65°	6

TABLE II (cont)

System	Substrate ^a	Catalyst ^b	Conditions ^c	Av # D in Product ^d
c			+ air, 14 hr, 65°	10
25a	1,12-C ₂ B ₁₀ H ₁₂	2,2-(PPh ₃) ₂ -2-H-2,1,7- RhC ₂ B ₉ H ₁₁	18 hr, 80°	6
b			a + 24 hr, 100°	10
26a	(2.0 mmol)	(0.10 mmol)	18 hr, 100°	6
b			37 hr, 100°	9
c			42 hr, 100°	10
27a	3-(η^5 -C ₅ H ₅)-3,1,2- CoC ₂ B ₉ H ₁₁	2,2-(PPh ₃) ₂ -2-H-2,1,7- RhC ₂ B ₉ H ₁₁	18 hr, 80°	6
b			a + 24 hr, 100°	6.1 ⁱ
28a ^h	B ₁₀ H ₁₄	2,2-(PPh ₃) ₂ -2-H-2,1,7- RhC ₂ B ₉ H ₁₁	18 hr, 80°	6
b ^h			a + 24 hr, 100°	7

TABLE III

Conditions for and Results of Selected Deuterium Exchange
Reactions Catalyzed by Other Species

System	Substrate ^a	Catalyst ^b	Conditions	Av # D in Product ^d
29	1,2-C ₂ B ₁₀ H ₁₂	(PPh ₃) ₃ RhCl ^e	18 hr, 80° ^f	2
30	(2.0 mmol)	10% Pd on C (1.0 g)	5 days, 100° ^f	2
31		Raney Ni (0.10 mmol)	36 hr, 100° ^f	Trace (C-D) ^g
32		Co(CN) ₅ D ³⁻ (1.0 mmol)	3 hr, 100° ^{f,h}	2 (C-D) ^g
33a	1,7-C ₂ B ₁₀ H ₁₂	(PPh ₃) ₂ (CO)IrCl	4 hr, 65°	1
b			24 hr, 65° then	
			20 hr, 100°	9
34			24 hr, 100°	10
35a		2-[(PPh ₃) ₂ IrHCl]- 1,7-C ₂ B ₁₀ H ₁₁	1 hr, 65°	3
b			4 hr, 65°	8
c			24 hr, 65°	10
36		[(PPh ₃) ₂ IrCl] ⁱ	20 hr, 40°	10
37		2-[(AsPh ₃) ₂ IrHCl]- 1,7-C ₂ B ₁₀ H ₁₁	20 hr, 40°	8

TABLE II (cont)

- a. 1.0 mmol, except where noted.
- b. 0.05 mmol, except where noted.
- c. In 20 ml toluene with D₂ bubbling at ca 3 cc/min and rapid stirring.
- d. Estimated from ir, mass, and ¹¹B nmr spectra.
- e. Deuterium gas not purified by BTS catalyst.
- f. After 20 hr at 65°, injected 0.56 ml (0.025 mmol) O₂ into D₂ inlet line.
- g. Reactor opened to atmosphere above condenser after 28 hr at 65°.
- h. Reaction with catalyst was observed.
- i. Deuterium also found in cyclopentadienyl ligand (see text).

TABLE III (cont)

System	Substrate ^a	Catalyst ^b	Conditions ^c	AV # D in Product ^d
38	1-P(CH ₃) ₂ -1,2-C ₂ B ₁₀ H ₁₁ (2.0 mmol)	II (0.10 mmol)	3 days, 100°	4
<p>a. Except where noted, 1.0 mmol.</p> <p>b. Except where noted, 0.05 mmol.</p> <p>c. In 20 ml toluene with D₂ bubbling at <u>ca</u> 3 cc/min and rapid stirring.</p> <p>d. Estimated from ir, mass and ¹¹B nmr spectra.</p> <p>e. Formed nearly insoluble dimer [(PPh₃)₂RhCl]₂, which slowly decomposed.</p> <p>f. Deuterium gas not purified by BTS catalyst.</p> <p>g. No trace of B-D found in ir spectrum.</p> <p>h. Two phase mixture of 10 ml D₂O and 2 ml toluene with D₂ bubbling at <u>ca</u> 3 ml/min. Catalyst was formed <u>in situ</u> from CoCl₂ + 6 KCN + D₂ before the substrate was introduced.</p> <p>i. Prepared <u>in situ</u> from [Ir(C₈H₁₄)₂Cl]₂ + 4 PPh₃.</p>				

TABLE IV
Mass Spectral Data for 3-(η^5 -C₅H₅)-3,1,2-CoC₂B₉H₁₁
and Deuterated Derivatives

Mass	3-(η^5 -C ₅ H ₅)-3,1,2-CoC ₂ B ₉ H ₁₁		Deuterated Products ^c	
	Theoretical ^a	Found ^b	System 10	System 27b
268			1.4	
267			5.9	0.3
266			26.2	2.7
265			53.7	20.3
264			82.2	70.3
263			100.0	100.0
262			62.2	83.9
261			39.6	53.4
260	0.12		17.2	19.5
259	3.85	2.0	7.8	6.3
258	49.88	47.1	2.5	2.5
257	100.00	100.0	1.0	1.1
256	94.58	91.1	0.3	0.7
255	52.99	54.1		
254	19.20	17.9		
253	4.56	3.5		
252	0.75	0.8		
251	0.08			
Mass average	256.32	256.31	263.13	262.51
127			4.8	
126	0.12		100.0	2.1
125	5.48	5.5	69.5	16.1
124	100.00	100.0	21.5	100.0
Mass average	124.05	124.05	125.45	124.17

a. Calculated by ISOTOPE.²⁴

b. Mass>250: Average of four spectra at 14eV, range of intensities = \pm 4%;
Mass<128: 70eV.

c. Mass>250: 15eV; Mass<128: 70eV.

Figure 1. The first reported oxidative addition involving a boron-hydrogen bond.⁴

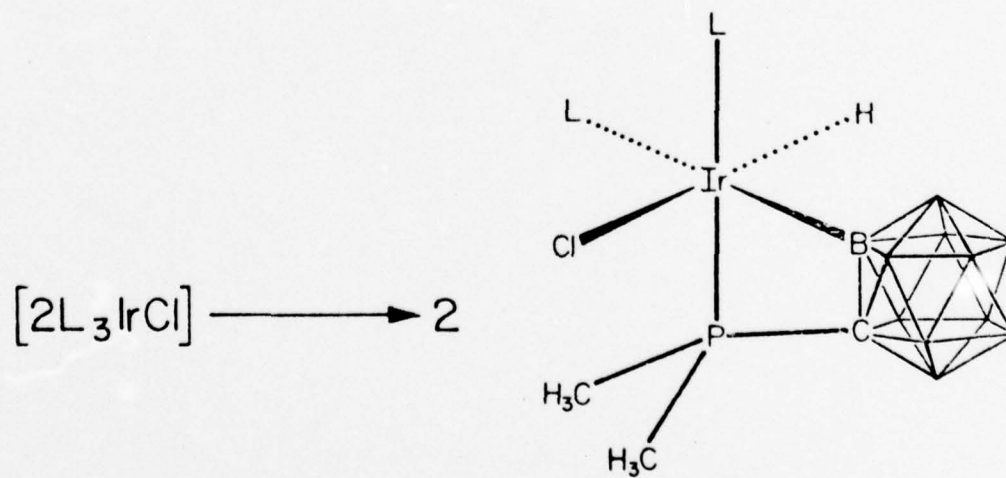
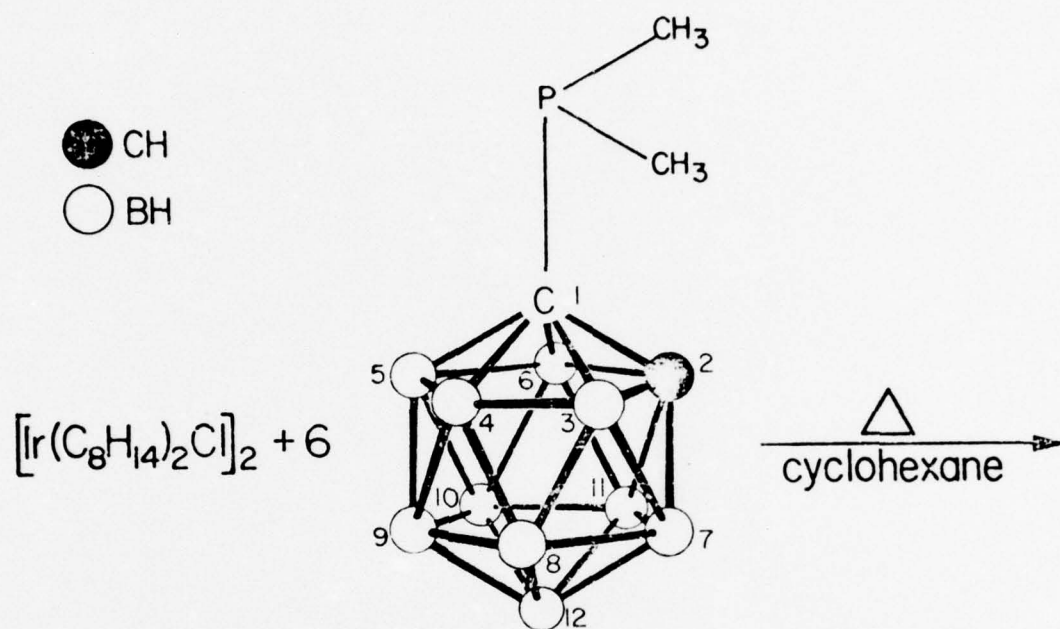


Figure 2. The 80.53 MHz ^{11}B nmr spectra of $1,2\text{-C}_{10}\text{H}_{12}$ taken in CH_2Cl_2 at various stages of deuterium exchange catalyzed by $(\text{PPh}_3)_3\text{RuHCl}$: a) no exchange; b) system 4; c) system 3; d) system 2; e) system 1b; f) no exchange, proton decoupled.

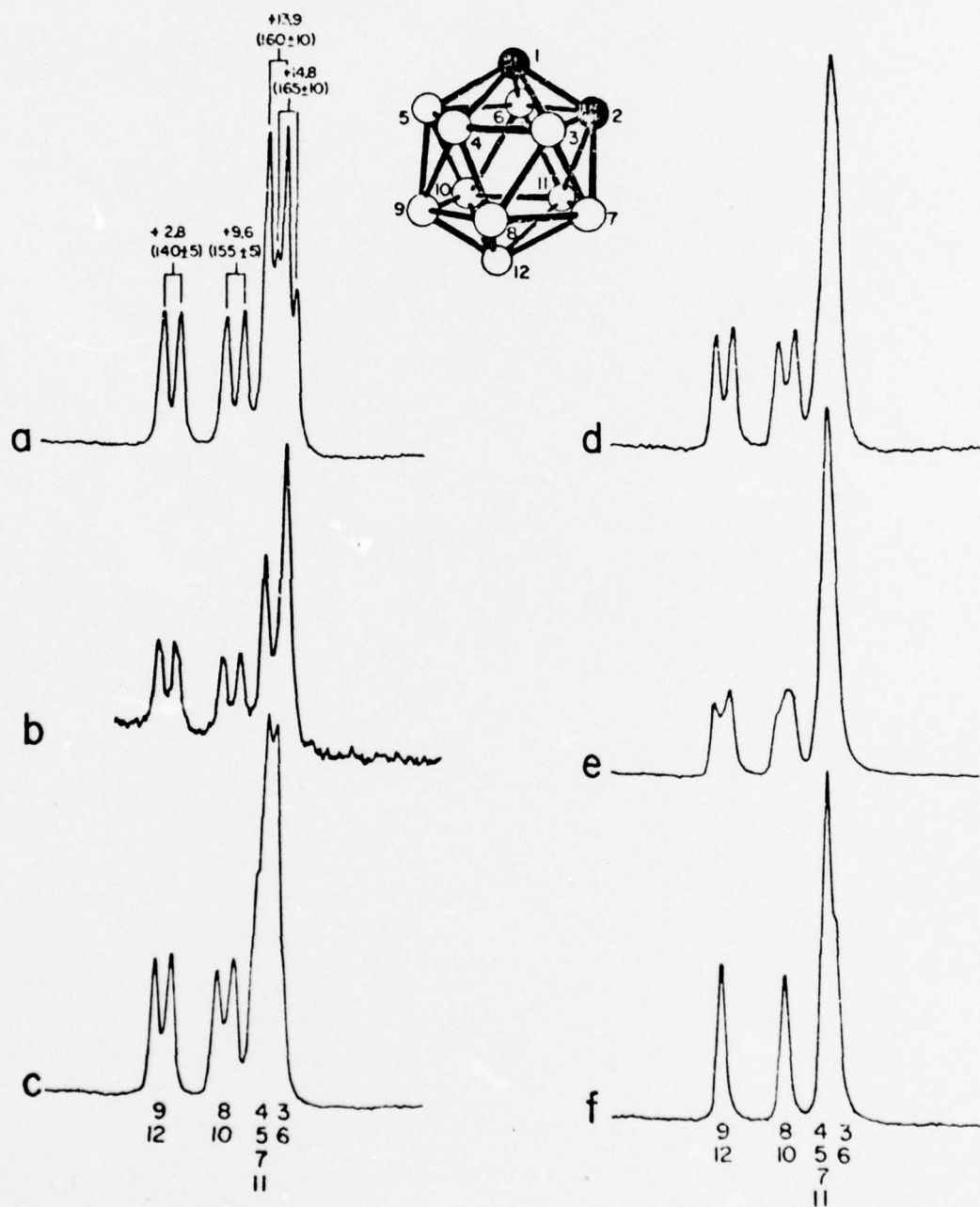


Figure 3. The 80.53 MHz ^{11}B nmr spectra of 1,7- $\text{C}_2\text{B}_{10}\text{H}_{12}$ at various stages of deuterium exchange catalyzed by $(\text{PPh}_3)_3\text{-RuHCl}$: a) no exchange, b) system 6, 2 hr; c) system 6a; d) system 6a + 3 hr, 100° ; e) system 6b; f) system 5. Spectra a and f taken in CH_2Cl_2 ; b-e taken in $\text{C}_6\text{H}_5\text{CH}_3$.

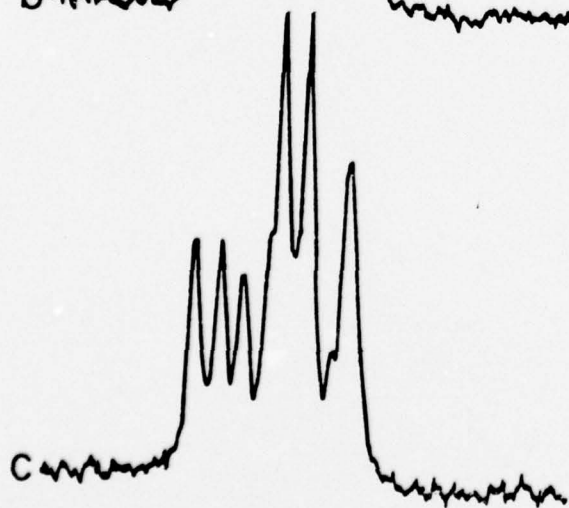
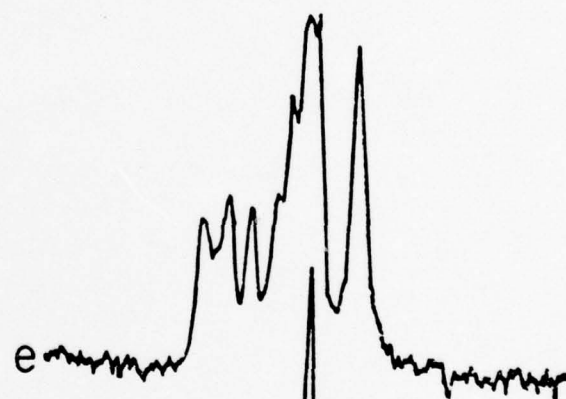
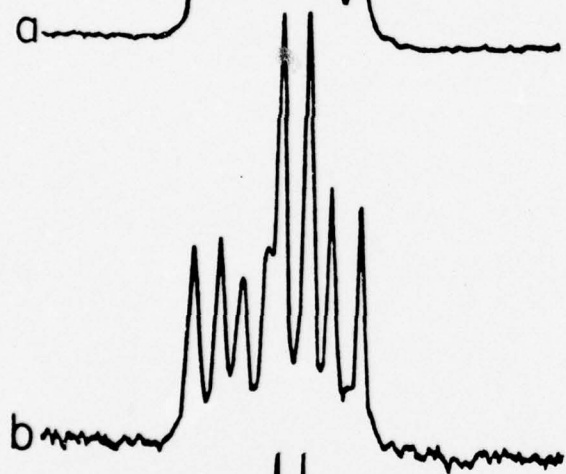
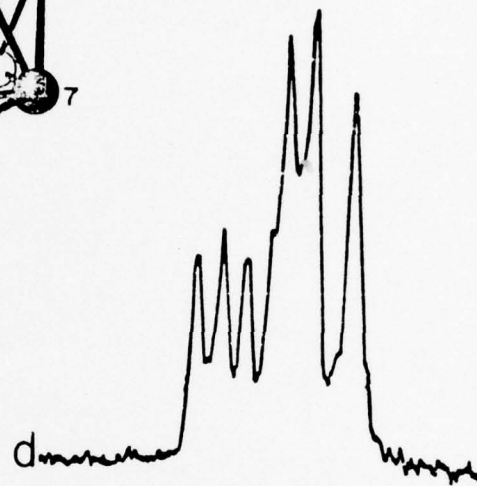
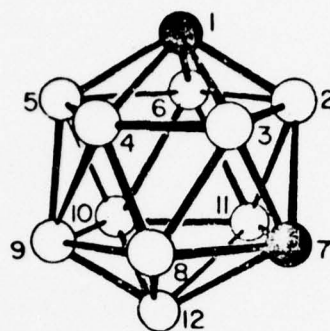
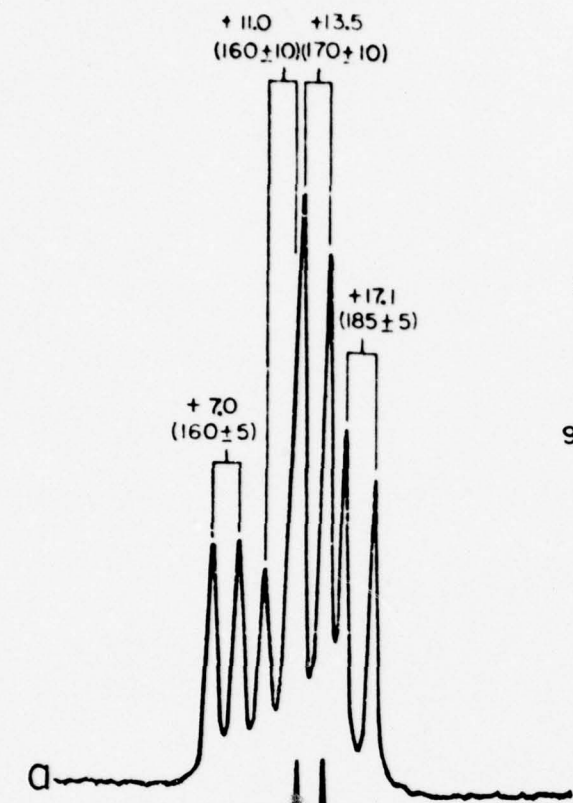
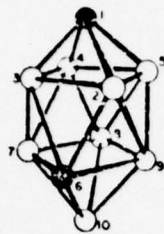


Figure 4. The 80.53 MHz ^{11}B nmr spectra of 1,6- $\text{C}_2\text{B}_8\text{H}_{10}$ at various stages of deuterium exchange catalyzed by $(\text{PPh}_3)_3\text{-RuHCl}$: a) no exchange; b) system 7, 2 hr; c) system 7, 4 hr; d) system 7, 20 hr; e) system 8; f) no exchange, proton decoupled. Spectra a,e,f taken in CCl_4 ; b-d taken in $\text{C}_6\text{H}_5\text{CH}_3$.



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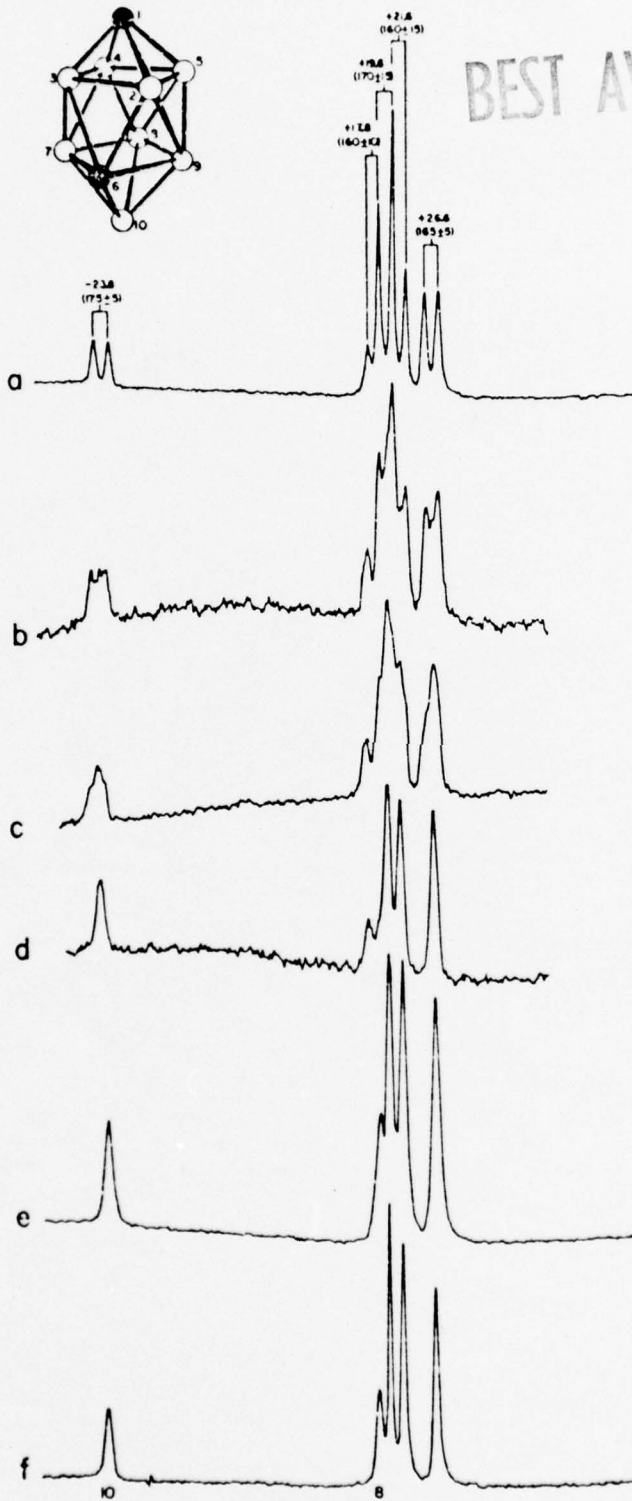


Figure 5. The 80.53 MHz ^{11}B nmr spectra of $1,7\text{-C}_2\text{B}_{10}\text{H}_{12}$ taken in $\text{C}_6\text{H}_5\text{CH}_3$ at various stages of deuterium exchange catalyzed by $3,3\text{-(PPh}_3)_2\text{-3-H-3,1,2-MC}_2\text{B}_9\text{H}_{11}$ ($\text{M} = \text{Rh, Ir}$). Spectra a-e are for $\text{M} = \text{Rh}$ and the products of the following systems: a) 19, 1 hr, 65° ; b) 19, 24 hr, 65° ; c) 19, 24 hr, 65° , then 3 hr, 100° ; d) 20d (illustrating rate enhancement effect of oxygen); e) 19b. Spectra f-j are for $\text{M} = \text{Ir}$ and the products of system 22 after: f) 1 hr, 65° ; g) 24 hr, 65° ; h) 24 hr, 65° , then 3 hr, 100° ; i) 24 hr, 65° , then 10 hr, 100° ; j) 22b.

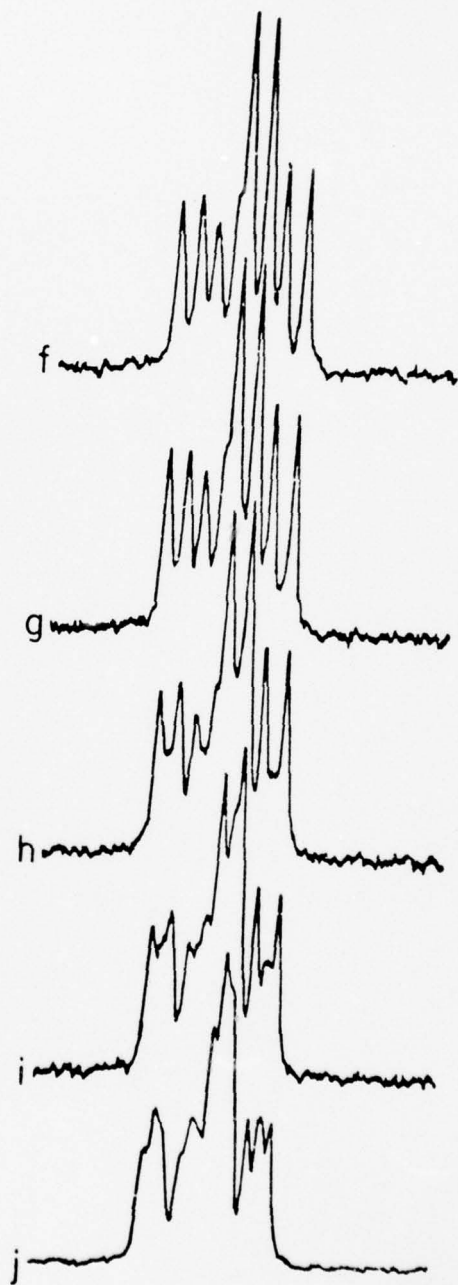
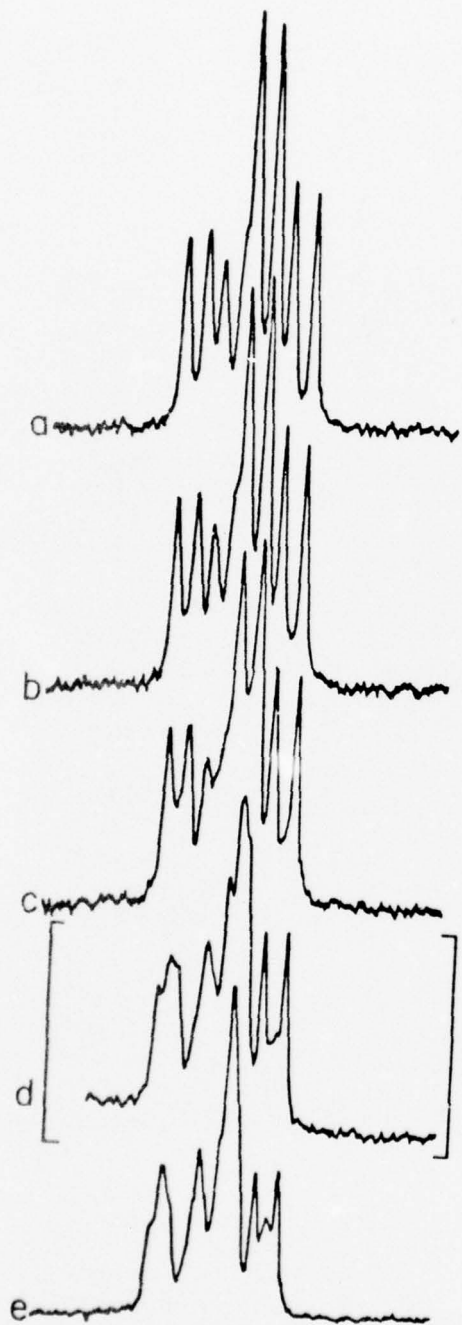


Figure 6. The 80.53 MHz ^{11}B nmr spectra of $1,7\text{-C}_2\text{B}_{10}\text{H}_{12}$ taken in $\text{C}_6\text{H}_5\text{CH}_3$ at various stages of deuterium exchange catalyzed by $2,2\text{-(PPh}_3)_2\text{-2-H-2,1,7-MC}_2\text{B}_9\text{H}_{11}$ ($\text{M} = \text{Rh, Ir}$). Spectra a-e are for $\text{M} = \text{Rh}$ and the products of system 21 after a) 1 hr; b) 4 hr; c) 8 hr; d) 20 hr; e) 21c. Spectra f-j are for $\text{M} = \text{Ir}$ and the products of system 24 after f) 1 hr; g) 4 hr; h) 8 hr; i) 20 hr; j) 24c.

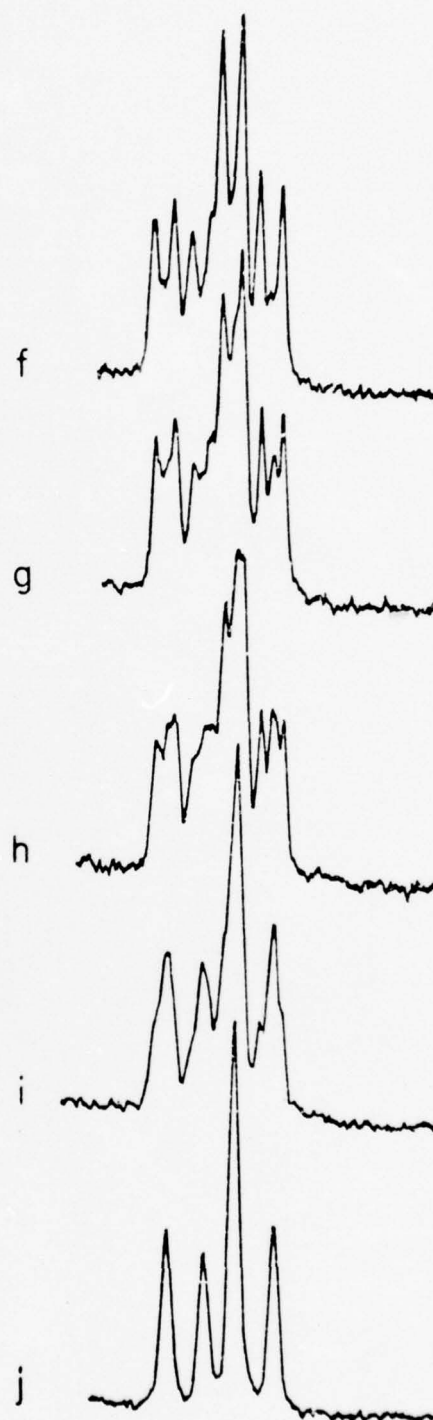
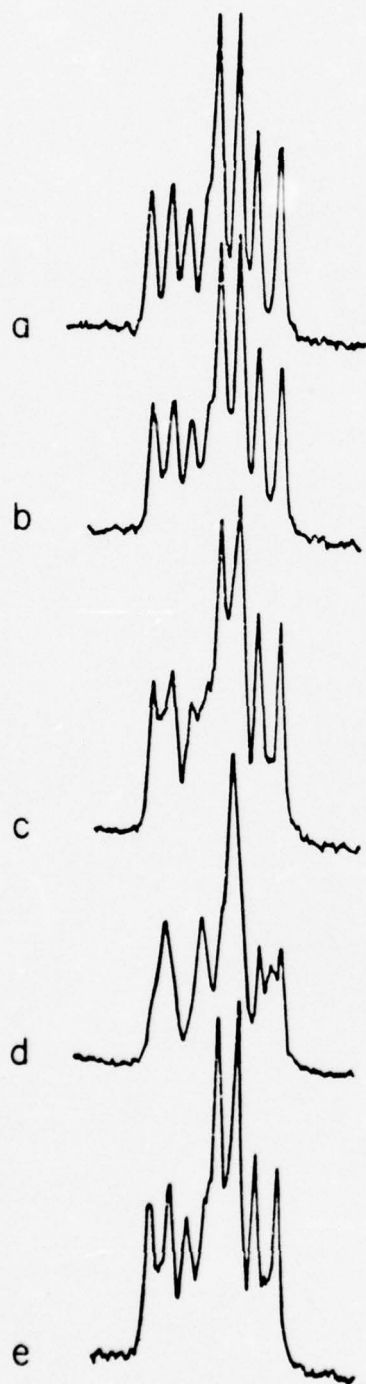


Figure 7. The 80.53 MHz ^{11}B nmr spectra of 1,7- $\text{C}_2\text{B}_{10}\text{H}_{12}$ taken in $\text{C}_6\text{H}_5\text{CH}_3$ at various stages of deuterium exchange catalyzed by $(\text{PPh}_3)_2(\text{CO})\text{IrCl}$. Spectra are of the products of system 33 after: a) 1 hr, 65°; b) 8 hr, 65°; c) 24 hr, 65°; d) 24 hr, 65°, then 3 hr, 100°; e) 24 hr, 65°, then 10 hr, 100°; f) 24 hr, 65°, then 20 hr, 100°.

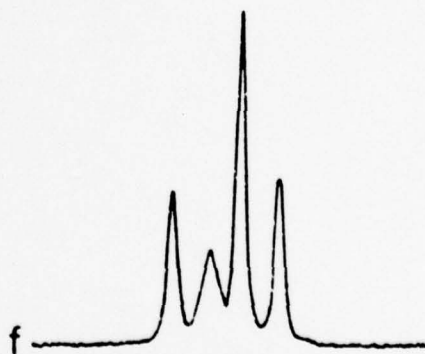
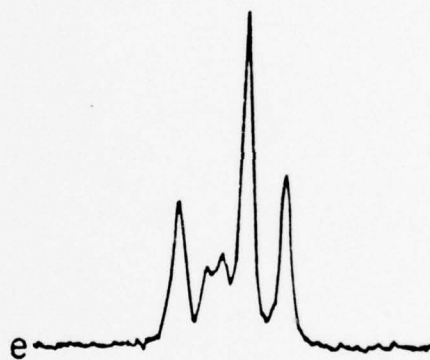
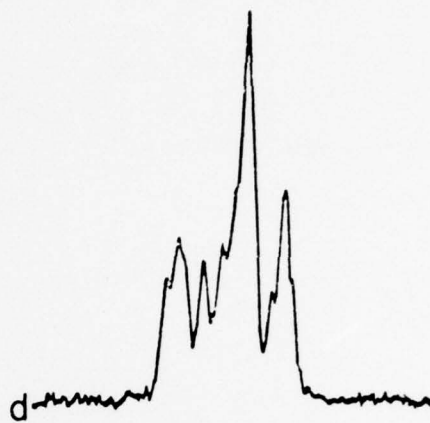
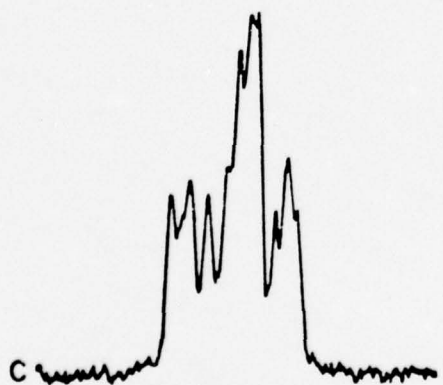
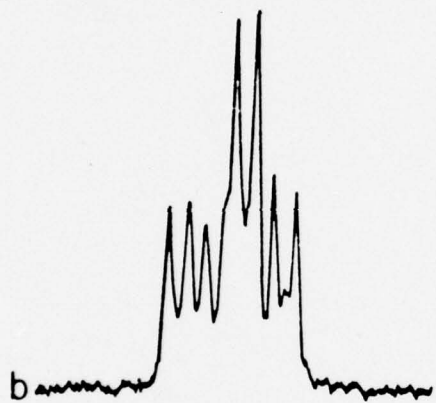
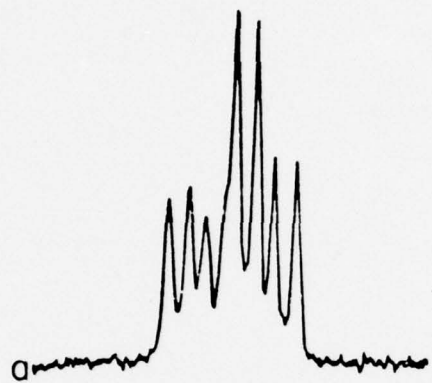


Figure 8. The 80.53 MHz ^{11}B nmr spectra of $1,7\text{-C}_2\text{B}_{10}\text{H}_{12}$ taken in $\text{C}_6\text{H}_5\text{CH}_3$ at various stages of deuterium exchange catalyzed by $(\text{PPh}_3)_2\text{IrCl}$ (a-e) and $2\text{-}[(\text{AsPh}_3)_2\text{Ir-HCl}]\text{-}1,7\text{-C}_2\text{B}_{10}\text{H}_{11}$ (f-g). Conditions for exchange were those of systems 36 and 37.

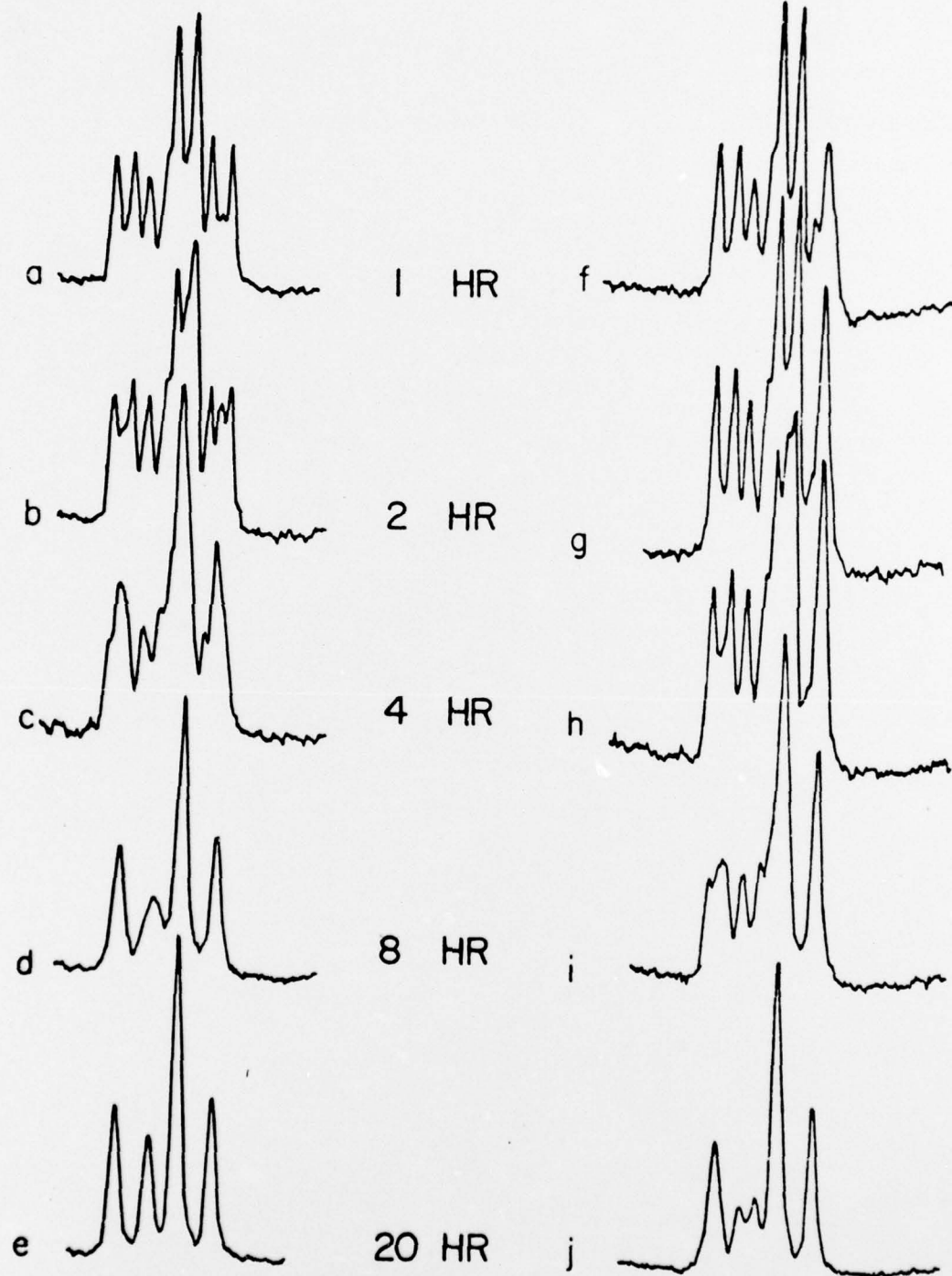


Figure 9. The 80.53 MHz ^{11}B nmr spectra of 3-($\eta^5\text{-C}_5\text{H}_5$)-3,1,2- $\text{CoC}_2\text{B}_9\text{H}_{11}$ at various stages of deuterium exchange catalyzed by $(\text{PPh}_3)_2\text{RuHCl}$ (b-d) and 2,2-(PPh_3) $_2$ -2-H-2,1,7- $\text{RhC}_2\text{B}_9\text{H}_{11}$ (e): a) no exchange; b) system 11, 1 hr; c) system 11, 2 hr; d) system 10; e) system 27b; f) no exchange, proton decoupled. Spectra b and c taken in $\text{C}_6\text{H}_5\text{CH}_3$, others in CH_2Cl_2 .

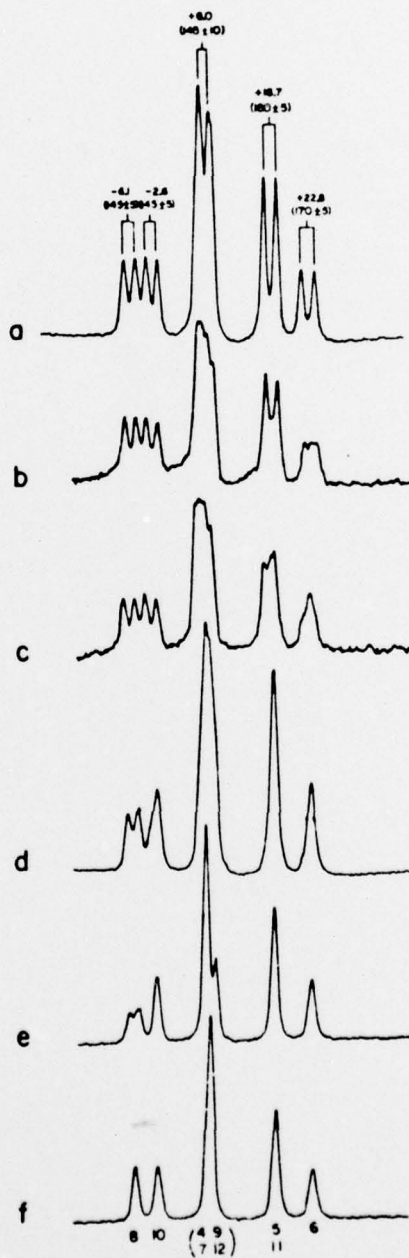
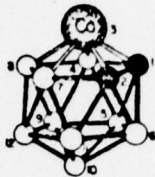


Figure 10. The 80.53 MHz ^{11}B nmr spectra of $\text{B}_{10}\text{H}_{14}$ taken in $\text{C}_6\text{H}_5\text{CH}_3$ at various stages of deuterium exchange catalyzed by $(\text{PPh}_3)_3\text{RuHCl}$ (b) and 2,2- $(\text{PPh}_3)_2$ -2-H-2,1,7- $\text{RhC}_2\text{B}_9\text{H}_{11}$ (c): a) no exchange; b) system 13b; c) system 27b; d) system 27b, proton decoupled.



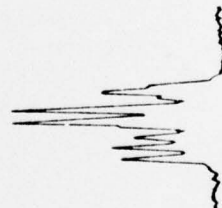
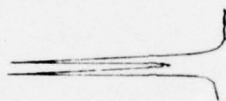
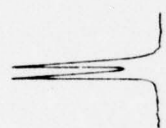
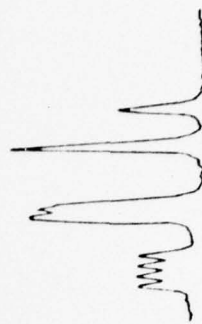
Figure 11. The 80.53 MHz ^{11}B nmr spectra of the products of deuterium exchange on the icosahedral substrates, as catalyzed by $(\text{PPh}_3)_3\text{RuHCl}$, under identical conditions (those of system 4).

3-(η^5 -C₅H₅)-3,1,2-CoC₂B₉H₁₁

1,12-C₂B₁₀H₁₂

1,7-C₂B₁₀H₁₂

1,2-C₂B₁₀H₁₂



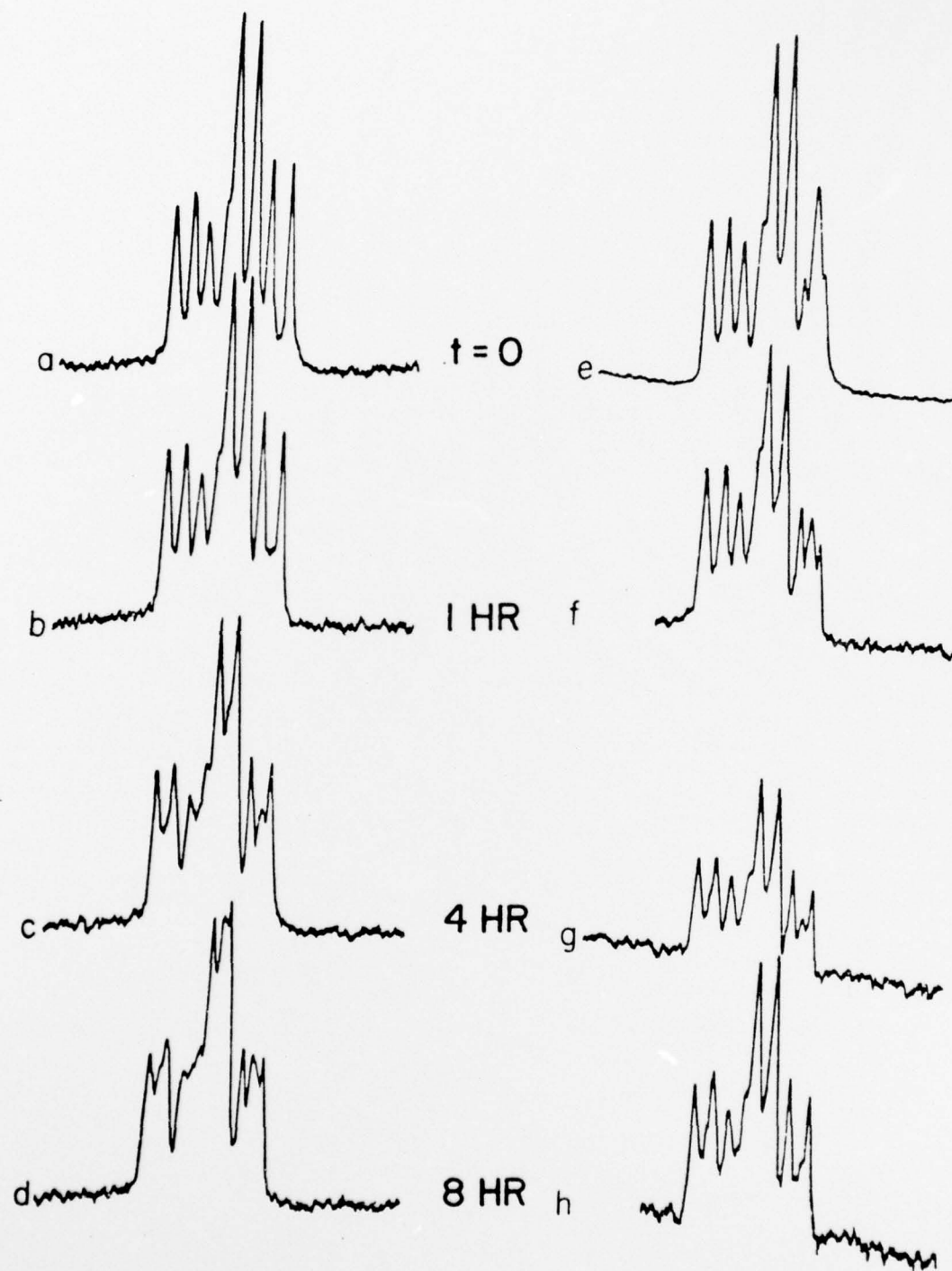
1 HR

2 HR

4 HR

20 HR

Figure 12. The 80.53 MHz ^{11}B nmr spectra of $1,7\text{-C}_2\text{B}_{10}\text{H}_{12}$ (a-d) and $2,3\text{-D}_2\text{-}1,7\text{-C}_2\text{B}_{10}\text{H}_{10}(\text{d}_1)$ (e-h) at various stages of deuterium exchange and deuterium scrambling, respectively, catalyzed by $2,2\text{-(PPh}_3)_2\text{-}2\text{-H-}2,1,7\text{-IrC}_2\text{B}_9\text{H}_{11}$. Conditions used were those of system 24 but without D_2 introduction for the scrambling.



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20. Abstract

A wide variety of substrates, including carboranes, metallocarboranes, and boron hydrides, were found to undergo catalytic isotopic exchange of terminal hydrogen with deuterium gas in the presence of various transition metal complexes. With $(PPh_3)_3RuHCl$ as catalyst, exchange was found to proceed with stereoselectivity indicative of nucleophilic attack at boron; e.g., the order of rates for deuterium incorporation at chemically non-equivalent sites in $1,2-C_2B_{10}H_{12}$ was $B(3,6) > B(4,5,7,11) > B(8,10) > B(9,12)$. Other catalysts, most notably the series of hydridometallocarboranes, $(PPh_3)_2HMC_2BgH_{11}$ ($M = Rh, Ir$), showed little or no stereoselectivity during deuterium exchange. Intermediate stereoselectivity was found with $(PPh_3)_2(CO)IrCl$ and $(PPh_3)_2IrCl$ species as catalysts, while exchange catalyzed by $(AsPh_3)_2IrCl$ exhibited the stereoselectivity found with $(PPh_3)_3RuHCl$. A mechanism is postulated which rationalizes the varied results and which involves oxidative addition of boron-hydrogen bonds to catalytic species.

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